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Applicant: IHARA CHEMICAL INDUSTRY CO., LTD.

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(Deposit Account No.) 066006

(Amount) Yen 21,000

(List of Annexed Documents)

(Item) Claims 1

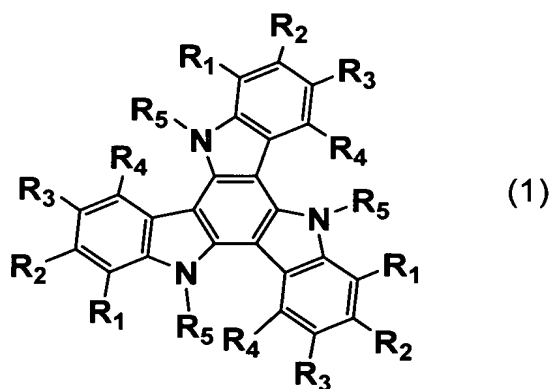
30 (Item) Specification 1

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(File Name) Claims

(Claim 1) A substituted Sym-triindole derivative represented by the following general formula (1)

[formula 1]



5 (wherein R₁, R₂, R₃ and R₄ are each independently hydrogen, halogen, C1-C6 alkyl group, C1-C6 haloalkyl group, substituted C1-C6 alkyl group, C2-C6 alkenyl group, substituted C2-C6 alkenyl group, C2-C6 alkynyl group, substituted C2-C6 alkynyl group, hydroxyl group, C1-C6 alkoxy group, aryloxy group, amino group, mono-substituted amino group, di-substituted amino group, acylamino group, mercapto group, C1-C6 alkylsulfenyl group, C1-C6 haloalkylsulfenyl group, arylsulfenyl group, substituted arylfenyl group, C1-C6 alkylsulfinyl group, C1-C6 haloalkylsulfinyl group, arylsulfinyl group, substituted arylsulfinyl group, C1-C6 alkylsulfonyl group, substituted arylsulfonyl group, C1-C6 alkylsulfonyl group,

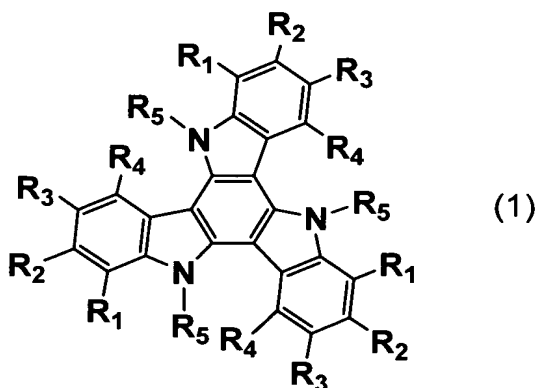
10

15

group, C1-C6 haloalkylsulfonyl group, arylsulfonyl group, substituted arylsulfonyl group, sulfonic acid group (hydroxy-sulfonyl group), aryl group, substituted aryl group, cyano group, nitro group, formyl group, acyl group, carboxyl group, 5 alkoxy carbonyl group, carbamoyl group, N-mono-substituted carbamoyl group, N,N-di-substituted carbamoyl group, hydrazonomethyl group (-CH=N-NH₂ group), N-mono-substituted hydrazonomethyl group, N,N-di-substituted hydrazonomethyl group, oximemethyl group (hydroxyiminomethyl group), alkoxyimi- 10 nomethyl group or aryloxyiminomethyl group; R₅ is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl group; in no event, all of R₁, R₂, R₃ and R₄ are hydrogen simultaneously).

(Claim 2) A process for producing a substituted Sym-triindole 15 derivative represented by the following general formula (1)

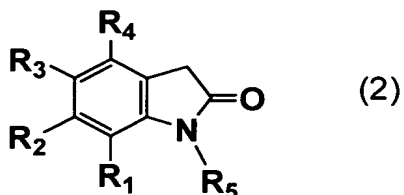
[formula 3]



(wherein R_1 , R_2 , R_3 and R_4 are each independently hydrogen, halogen, C1-C6 alkyl group, C1-C6 haloalkyl group, substituted C1-C6 alkyl group, C2-C6 alkenyl group, substituted C2-C6 alkenyl group, C2-C6 alkynyl group, substituted C2-C6 alkynyl group, hydroxyl group, C1-C6 alkoxy group, aryloxy group, amino group, mono-substituted amino group, di-substituted amino group, acylamino group, mercapto group, C1-C6 alkylsulfenyl group, C1-C6 haloalkylsulfenyl group, arylsulfenyl group, substituted arylsulfenyl group, C1-C6 alkylsulfinyl group, C1-C6 haloalkylsulfinyl group, arylsulfinyl group, substituted arylsulfinyl group, C1-C6 alkylsulfonyl group, C1-C6 haloalkylsulfonyl group, arylsulfonyl group, substituted arylsulfonyl group, sulfonic acid group (hydroxy-sulfonyl group), aryl group, substituted aryl group, cyano group, nitro group, formyl group, acyl group, carboxyl group,

alkoxycarbonyl group, carbamoyl group, N-mono-substituted carbamoyl group, N,N-di-substituted carbamoyl group, hydrazonomethyl group (-CH=N-NH₂ group), N-mono-substituted hydrazonomethyl group, N,N-di-substituted hydrazonomethyl group, oximemethyl group (hydroxyiminomethyl group), alkoxyiminomethyl group or aryloxyiminomethyl group; R₅ is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl group; in no event, all of R₁, R₂, R₃ and R₄ are hydrogen simultaneously), which process comprises reacting a substituted oxyindole represented by the following general formula (2)

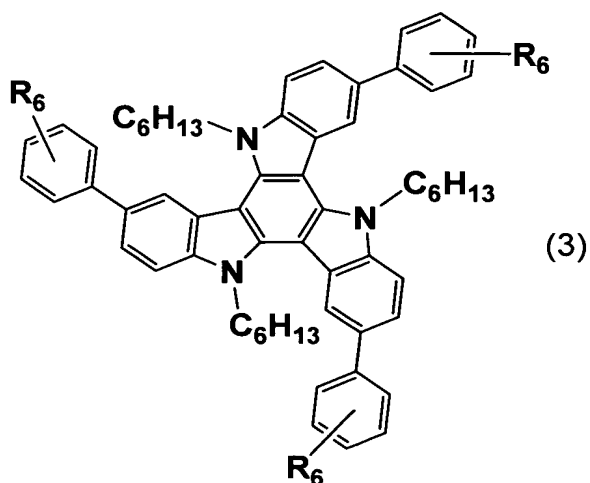
[formula 2]



(wherein R₁, R₂, R₃, R₄ and R₅ have the same definitions as given above) with a phosphorus oxyhalide.

(Claim 3) A Sym-triindole derivative represented by the following general formula (3)

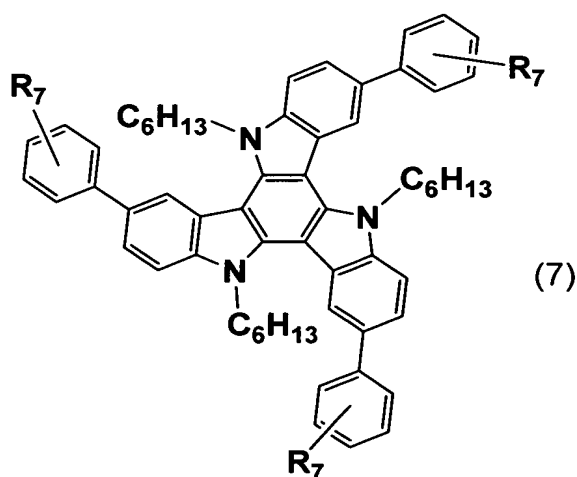
[formula 4]



(wherein R_6 is hydrogen, formyl group, cyano group, ester group or dicyanovinyl group, and $-C_6H_{13}$ is n-hexyl group).

(Claim 4) A process for producing a Sym-triindole derivative represented by the following general formula (7)

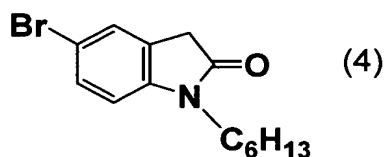
5 [formula 8]



(wherein R_7 is hydrogen, formyl group, cyano group or ester group, and $-C_6H_{13}$ is n-hexyl group), which process comprises

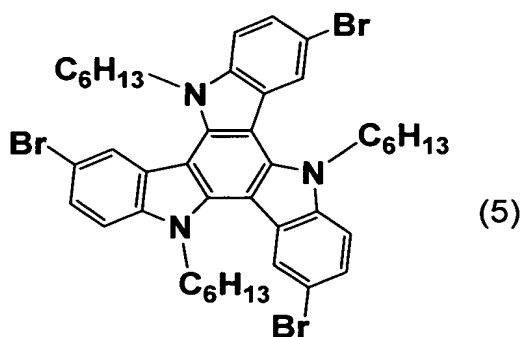
reacting an N-(n-hexyl)-5-bromooxyindole represented by the following general formula (4)

[formula 5]



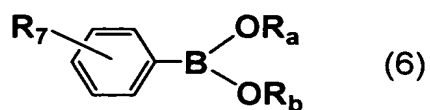
(wherein -C₆H₁₃ is n-hexyl group) with a phosphorus oxyhalide
5 to obtain an N-(n-hexyl)-5-bromotriindole derivative represented by the following general formula (5)

[formula 6]



(wherein -C₆H₁₃ has the same definition as given above) and
further reacting it with a boric acid compound represented by
10 the following general formula (6)

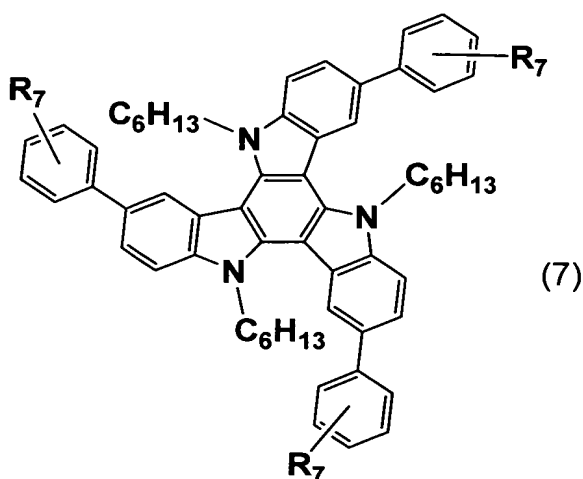
[formula 7]



(wherein R_7 has the same definition as give above; and R_a and R_b are each independently hydrogen atom, C1-C6 alkyl group or optionally substituted phenyl group and may be combined to each other to form a ring).

5 (Claim 5) A process for producing a Sym-triindole derivative represented by the following general formula (7)

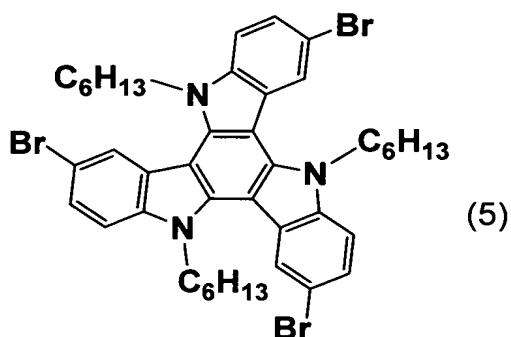
[formula 11]



(wherein R_7 is hydrogen, formyl group, cyano group or ester group , and $-C_6H_{13}$ is n-hexyl group), which process comprises

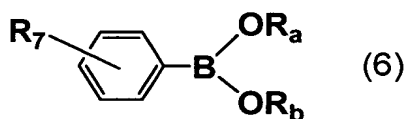
10 reacting an N-(n-hexyl)-5-bromotriindole derivative represented by the following general formula (5)

[formula 9]



(wherein $-C_6H_{13}$ has the same definition as give above) with a boric acid compound represented by the following general formula (6)

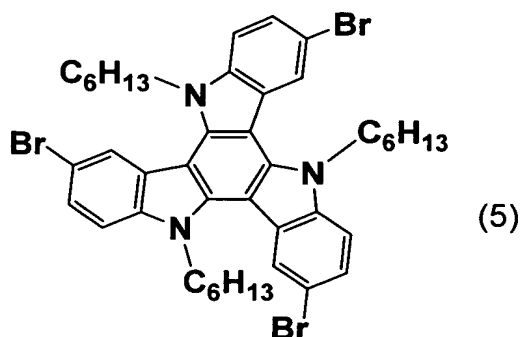
[formula 10]



5 (wherein R_7 has the same definition as given above; and R_a and R_b are each independently hydrogen atom, C1-C6 alkyl group or optionally substituted phenyl group and may be combined to each other to form a ring).

(Claim 6) A process for producing an N-(n-hexyl)-5-bromotriindole derivative represented by the following general formula (5)

[formula 13]



(wherein $\text{-C}_6\text{H}_{13}$ is n-hexyl group), which process comprises reacting an N-(n-hexyl)-5-bromooxyindole represented by the following general formula (4)

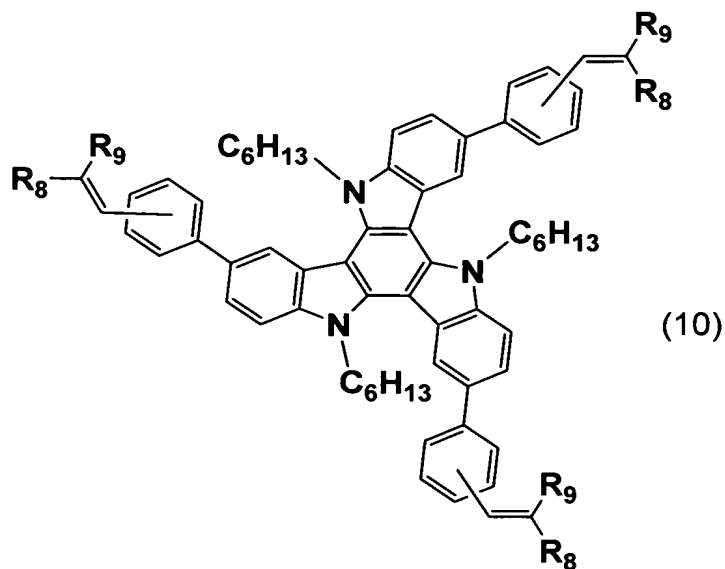
[formula 12]



5 with a phosphorus oxyhalide.

(Claim 7) A process for producing a Sym-triindole derivative represented by the following general formula (10)

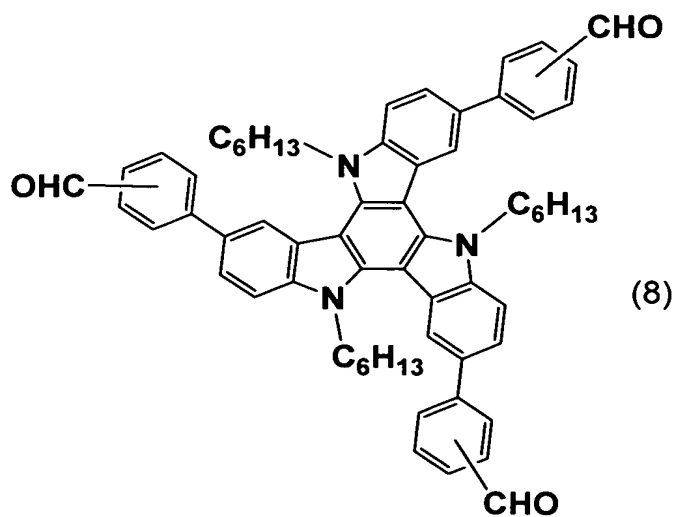
[formula 16]



(wherein R_8 is hydrogen or cyano group; R_9 is cyano group, carboxylic acid group, alkoxy carbonyl group, aryl group or substituted aryl group; and $-\text{C}_6\text{H}_{13}$ is n-hexyl group), which process comprises reacting a triindole derivative represented

5 by the following general formula (8)

[formula 14]



(wherein $-C_6H_{13}$ has the same definition as given above) with a methylene compound represented by the general formula (9)

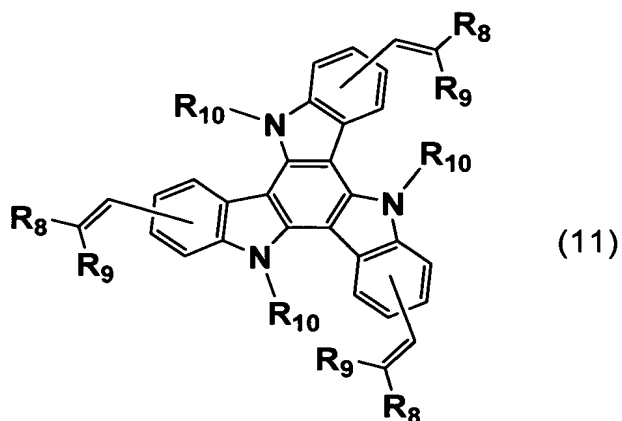
[formula 15]



(wherein R_8 and R_9 have the same definitions as give above).

5 (Claim 8) A Sym-triindole vinyl derivative represented by the following general formula (11)

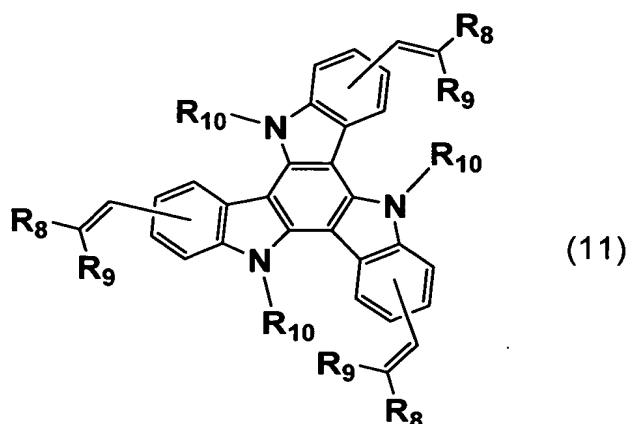
[formula 17]



(wherein R_8 is hydrogen or cyano group; R_9 is cyano group, carboxylic acid group, ester group, aryl group or substituted
10 aryl group; and R_{10} is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl group).

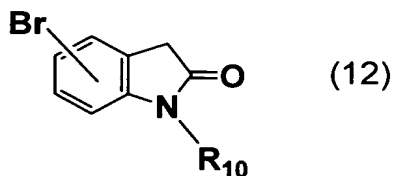
(Claim 9) A process for producing a Sym-triindole derivative represented by the following general formula (11)

[formula 22]



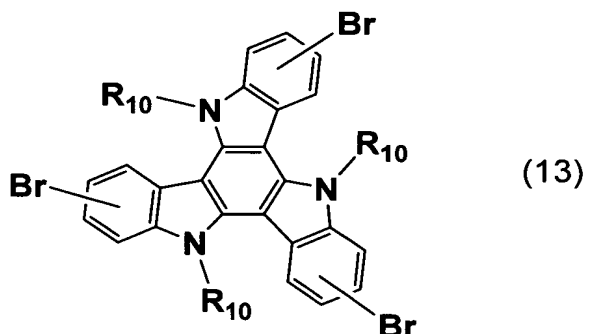
(wherein R_8 is hydrogen or cyano group; R_9 is cyano group, carboxylic acid group, ester group, aryl group or substituted aryl group; and R_{10} is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl group), which process comprises reacting an oxyindole compound represented by the following general formula (12)

[formula 18]



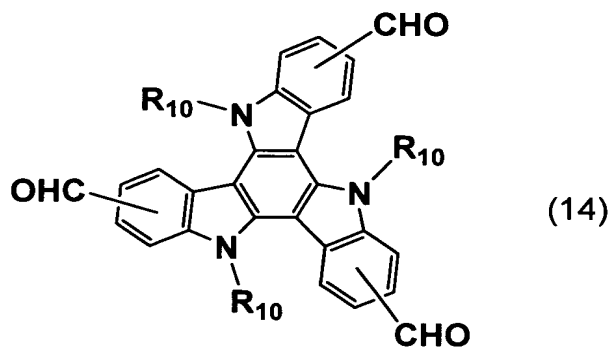
(wherein R_{10} is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl group) with a phosphorus oxyhalide to obtain a Sym-bromotriindole derivative represented by the following general formula (13)

[formula 19]



(wherein R_{10} has the same definition as given above), sub-
jecting it to formylation with a formylating agent in the
presence of butyllithium to obtain a Sym-formyltriindole de-
5 rivative represented by the following general formula (14)

[formula 20]



(wherein R_{10} has the same definition as given above), and re-
acting it with a methylene compound represented by the fol-
lowing general formula (9)

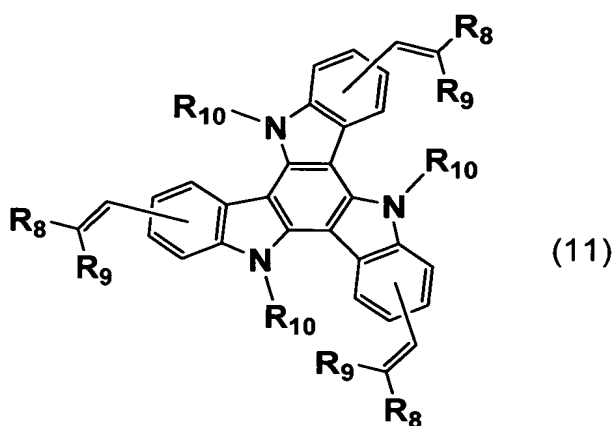
10 [formula 21]



(wherein R₈ and R₉ have the same definitions as given above).

(Claim 10) A process for producing a Sym-triindole derivative represented by the following general formula (11)

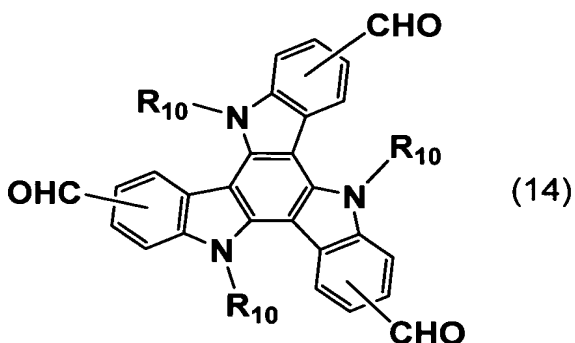
[formula 25]



5 (wherein R₈ is hydrogen or cyano group; R₉ is cyano group, carboxylic acid group, alkoxycarbonyl group, aryl group or substituted aryl group; and R₁₀ is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl group), which process comprises reacting a Sym-formyltriindole derivative

10 represented by the following general formula (14)

[formula 23]



(wherein R_{10} has the same definition as given above) with a methylene compound represented by the following general formula (9)

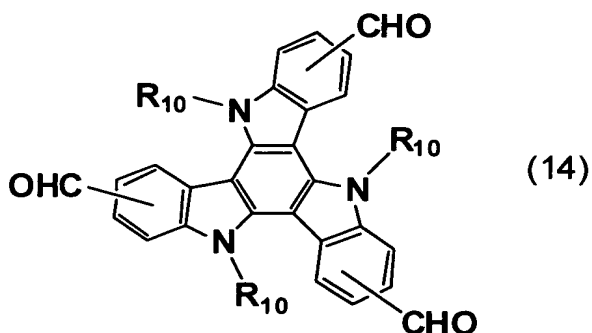
[formula 24]



5 (wherein R_8 and R_9 have the same definitions as given above).

(Claim 11) A process for producing a Sym-formyltriindole derivative represented by the following general formula (14)

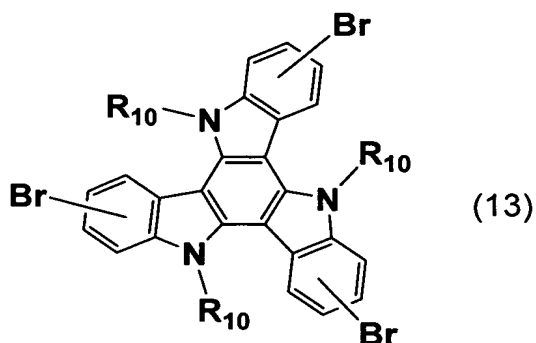
[formula 27]



(wherein R_{10} is C2-C12 alkyl group, C2-C12 substituted alkyl
 10 group or C2-C12 haloalkyl group), which process comprises

subjecting a Sym-bromotriindole derivative represented by the following general formula (13)

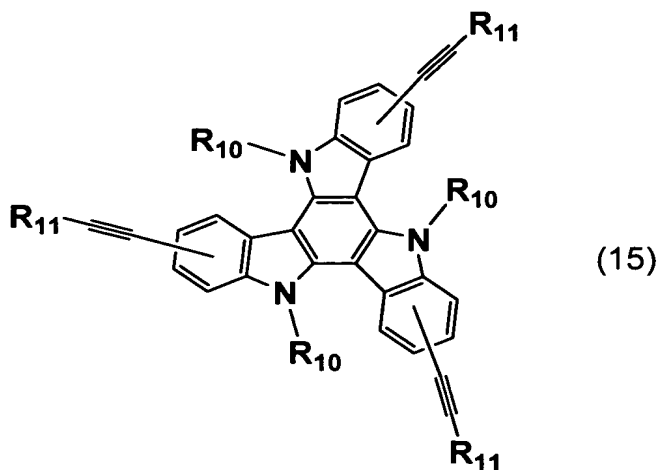
[formula 26]



(wherein R₁₀ has the same definition as given above), to formylation with a formylating agent in the presence of butyllithium.

(Claim 12) A Sym-triindole derivative represented by the following general formula (15)

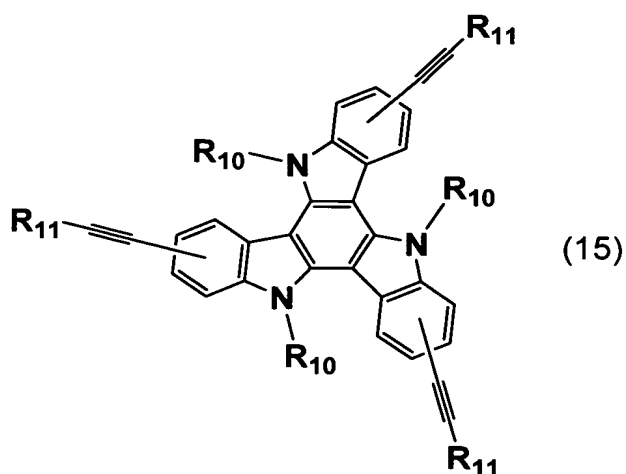
[formula 28]



(wherein R_{10} is C2-C12 alkyl group, C2-C12 substituted alkyl group or C2-C12 haloalkyl group; and R_{11} is aryl group or substituted aryl group).

(Claim 13) A process for producing a Sym-triindole derivative represented by the following general formula (15)

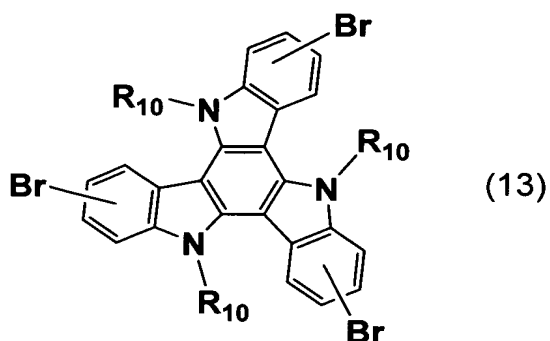
[formula 31]



(wherein R_{10} is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl group; and R_{11} is aryl group or substituted aryl group), which process comprises reacting a

10 Sym-bromotriindole derivative represented by the following general formula (13)

[formula 29]



(wherein R_{10} has the same definition as given above) with an acetylene derivative represented by the following general formula (16)

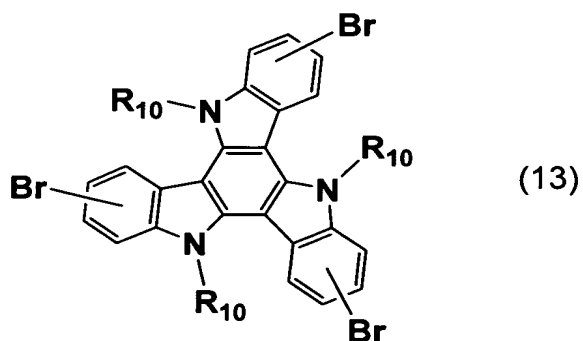
[formula 30]



5 (wherein R_{11} has the same definition as given above and R_{12} is hydrogen or trimethylsilyl group).

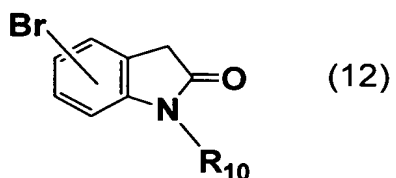
(Claim 14) A process for producing a Sym-bromotriindole derivative represented by the following general formula (16)

[formula 33]



(wherein R_{10} is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl group), which process comprises reacting an oxyindole compound represented by the following general formula (12)

5 [formula 32]



(wherein R_{10} has the same definition as given above).

(File Name) Description

(Title of the Invention) Substituted Sym-triindole

(Technical Field)

[0001]

5 The present invention provides a novel substituted Sym-triindole derivative and a process for production thereof. The substituted Sym-triindole derivative of the present invention is applicable to a wide spectrum of uses, such as various electrification preventions, electrification controls, capacitors, batteries, chemical sensors, displays, organic EL materials, solar cells, photodiodes, phototransistors, non-linear materials, photorefractive materials, rustproof agents, adhesives, fibers, antistatic paints, electrodeposition paints, plating primers, electric corrosion protections and
10 the like.
15

(Background Art)

[0002]

Di-substituted Sym-triindole derivatives are reported. However, with the synthesis process therefor, it has been
20 difficult to synthesize a tri- or higher-substituted Sym-

triindole derivative. (See Patent Literature 1.)

[0003]

Patent Literature 1: JP-A-2000-105139

(Disclosure of the Invention)

5 (Task to Be Achieved by the Invention)

[0004]

The present invention aims at providing a novel substituted Sym-triindole derivative which is applicable to a wide spectrum of uses, such as various electrification preventions, electrification controls, capacitors, batteries, chemical
10 sensors, displays, organic EL materials, solar cells, photodiodes, phototransistors, nonlinear materials, photorefractive materials, rustproof agents, adhesives, fibers, antistatic paints, electrodeposition paints, plating primers, electric corrosion protections and the like.

(Means for Achieving the Task)

[0005]

In view of the above-mentioned situation, the present inventor made a study on the process for producing a substituted Sym-triindole derivative. As a result, it was found
20

unexpectedly that, by reacting a substituted oxyindole with a phosphorus oxyhalide such as phosphorus oxychloride or the like, a tri- or higher-substituted Sym-triindole derivative can be synthesized selectively, that is, the above-mentioned
5 task can be achieved. The finding has led to the completion of the present invention.

(Effect of the Invention)

[0006]

By the process of the present invention, there can be
10 provided a novel substituted Sym-triindole derivative which is applicable to a wide spectrum of uses, such as various electrification preventions, electrification controls, capacitors, batteries, chemical sensors, displays, organic EL materials, solar cells, photodiodes, phototransistors, non-
15 linear materials, photorefractive materials, rustproof agents, adhesives, fibers, antistatic paints, electrodeposition paints, plating primers, electric corrosion protections and the like.

[Best Mode for Carrying out the Invention]

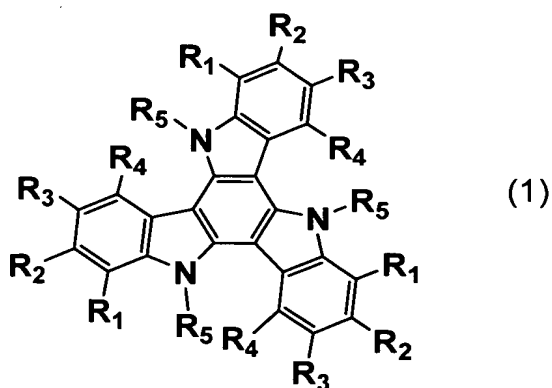
20 [0007]

The present invention is described in detail below.
 The present invention provides inventions described in the
 following [1] to [14].

[0008] to [0011]

5 [1] A substituted Sym-triindole derivative represented by
 the following general formula (1)

[formula 1]



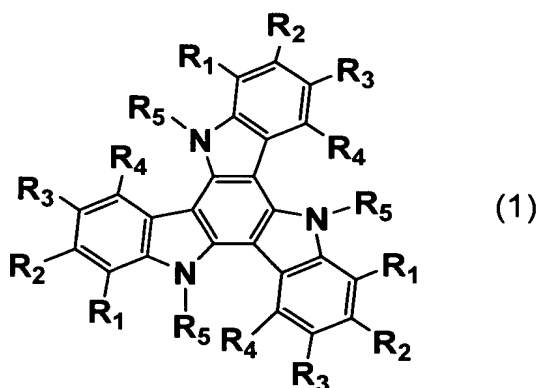
(wherein R₁, R₂, R₃ and R₄ are each independently hydrogen,
 halogen, C1-C6 alkyl group, C1-C6 haloalkyl group, substi-
 10 tuted C1-C6 alkyl group, C2-C6 alkenyl group, substituted C2-
 C6 alkenyl group, C2-C6 alkynyl group, substituted C2-C6 al-
 kynyl group, hydroxyl group, C1-C6 alkoxy group, aryloxy
 group, amino group, mono-substituted amino group, di-
 substituted amino group, acylamino group, mercapto group, C1-
 15 C6 alkylsulfenyl group, C1-C6 haloalkylsulfenyl group, aryl-

sulphenyl group, substituted arylphenyl group, C1-C6 alkylsulfinyl group, C1-C6 haloalkylsulfinyl group, arylsulfinyl group, substituted arylsulfinyl group, C1-C6 alkylsulfonyl group, C1-C6 haloalkylsulfonyl group, arylsulfonyl group, substituted arylsulfonyl group, sulfonic acid group (hydroxy-sulfonyl group), aryl group, substituted aryl group, cyano group, nitro group, formyl group, acyl group, carboxyl group, alkoxy-carbonyl group, carbamoyl group, N-mono-substituted carbamoyl group, N,N-di-substituted carbamoyl group, hydrazo-
10 nomethyl group ($-\text{CH}=\text{N}-\text{NH}_2$ group), N-mono-substituted hydrazo-
nomethyl group, N,N-di-substituted hydrazonomethyl group, oximemethyl group (hydroxyiminomethyl group), alkoxyimi-
nomethyl group or aryloxyiminomethyl group; R_5 is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl
15 group; in no event, all of R_1 , R_2 , R_3 and R_4 are hydrogen simultaneously).

[0012] to [0018]

[2] A process for producing a substituted Sym-triindole derivative represented by the following general formula (1)

20 [formula 3]

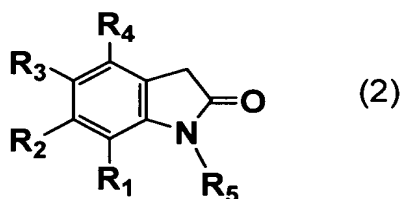


(wherein R_1 , R_2 , R_3 and R_4 are each independently hydrogen, halogen, C1-C6 alkyl group, C1-C6 haloalkyl group, substituted C1-C6 alkyl group, C2-C6 alkenyl group, substituted C2-C6 alkenyl group, C2-C6 alkynyl group, substituted C2-C6 alkynyl group, hydroxyl group, C1-C6 alkoxy group, aryloxy group, amino group, mono-substituted amino group, di-substituted amino group, acylamino group, mercapto group, C1-C6 alkylsulfenyl group, C1-C6 haloalkylsulfenyl group, arylsulfenyl group, substituted arylfenyl group, C1-C6 alkylsulfinyl group, C1-C6 haloalkylsulfinyl group, arylsulfinyl group, substituted arylsulfinyl group, C1-C6 alkylsulfonyl group, C1-C6 haloalkylsulfonyl group, arylsulfonyl group, substituted arylsulfonyl group, sulfonic acid group (hydroxy-sulfonyl group), aryl group, substituted aryl group, cyano group, nitro group, formyl group, acyl group, carboxyl group,

alkoxycarbonyl group, carbamoyl group, N-mono-substituted carbamoyl group, N,N-di-substituted carbamoyl group, hydrazonomethyl group (-CH=N-NH₂ group), N-mono-substituted hydrazonomethyl group, N,N-di-substituted hydrazonomethyl group, oximemethyl group (hydroxyiminomethyl group), alkoxyiminomethyl group or aryloxyiminomethyl group; R₅ is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl group; in no event, all of R₁, R₂, R₃ and R₄ are hydrogen simultaneously), which process comprises reacting a substituted

oxyindole represented by the following general formula (2)

[formula 2]

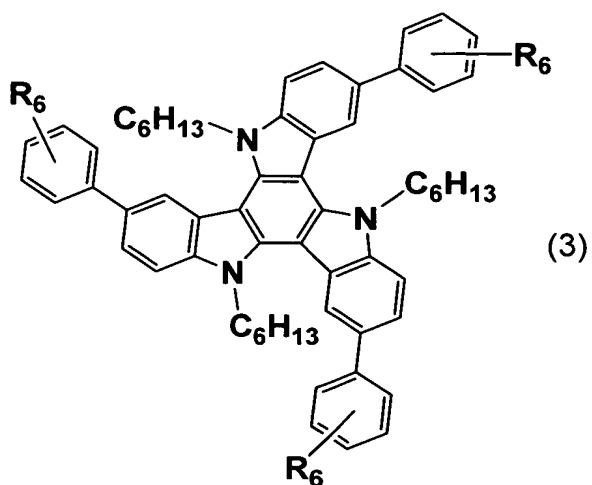


(wherein R₁, R₂, R₃, R₄ and R₅ have the same definitions as given above) with a phosphorus oxyhalide.

[0019] to [0022]

[3] A Sym-triindole derivative represented by the following general formula (3)

[formula 4]

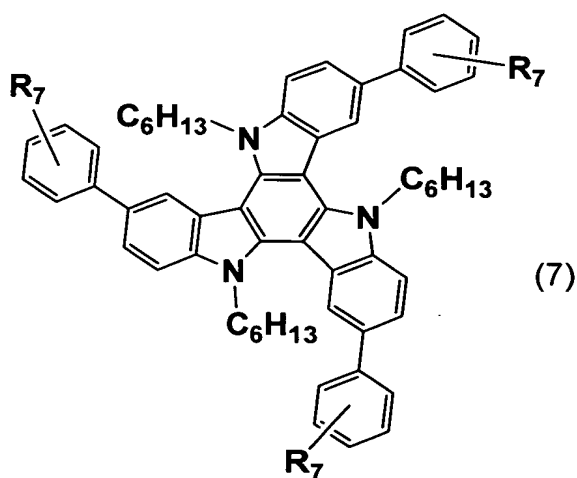


(wherein R_6 is hydrogen, formyl group, cyano group, ester group or dicyanovinyl group, and $-C_6H_{13}$ is n-hexyl group).

[0023] to [0035]

[4] A process for producing a Sym-triindole derivative represented by the following general formula (7)

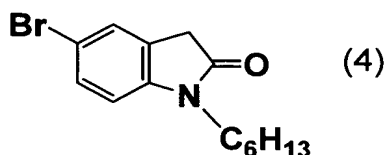
[formula 8]



(wherein R_7 is hydrogen, formyl group, cyano group or ester

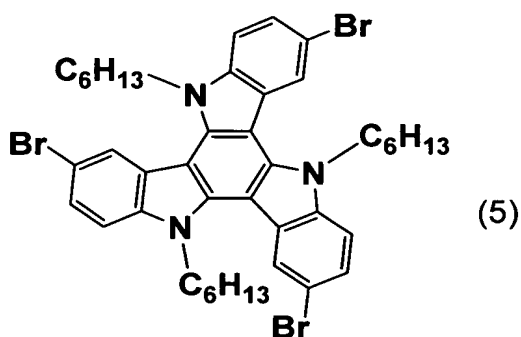
group, and $-C_6H_{13}$ is n-hexyl group), which process comprises reacting an N-(n-hexyl)-5-bromooxyindole represented by the following general formula (4)

[formula 5]



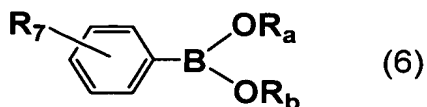
5 (wherein $-C_6H_{13}$ is n-hexyl group) with a phosphorus oxyhalide to obtain an N-(n-hexyl)-5-bromotriindole derivative represented by the following general formula (5)

[formula 6]



(wherein $-C_6H_{13}$ has the same definition as given above) and
 10 further reacting it with a boric acid compound represented by the following general formula (6)

[formula 7]

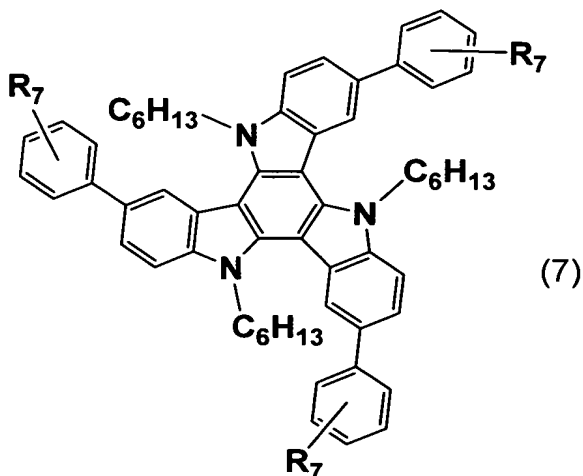


(wherein R₇ has the same definition as give above; and R_a and R_b are each independently hydrogen atom, C1-C6 alkyl group or optionally substituted phenyl group and may be combined to each other to form a ring).

5 [0036] to [0045]

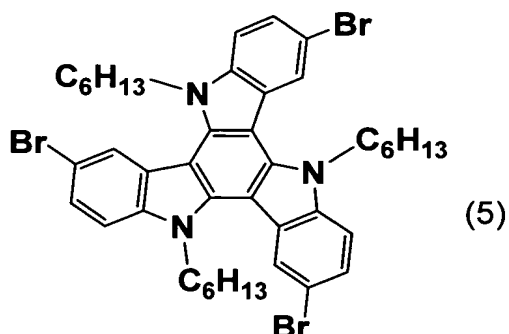
[5] A process for producing a Sym-triindole derivative represented by the following general formula (7)

[formula 11]



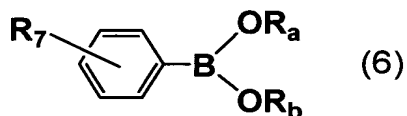
(wherein R₇ is hydrogen, formyl group, cyano group or ester
 10 group , and -C₆H₁₃ is n-hexyl group), which process comprises reacting an N-(n-hexyl)-5-bromotriindole derivative represented by the following general formula (5)

[formula 9]



(wherein $-C_6H_{13}$ has the same definition as give above) with a boric acid compound represented by the following general formula (6)

5 [formula 10]

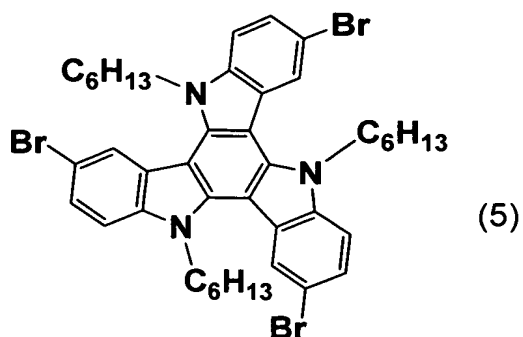


(wherein R_7 has the same definition as given above; and R_a and R_b are each independently hydrogen atom, C1-C6 alkyl group or optionally substituted phenyl group and may be combined to each other to form a ring).

10 [0046] to [0051]

[6] A process for producing an N-(n-hexyl)-5-bromotriindole derivative represented by the following general formula (5)

[formula 13]



(wherein $\text{-C}_6\text{H}_{13}$ is n-hexyl group), which process comprises reacting an N-(n-hexyl)-5-bromooxyindole represented by the following general formula (4)

[formula 12]

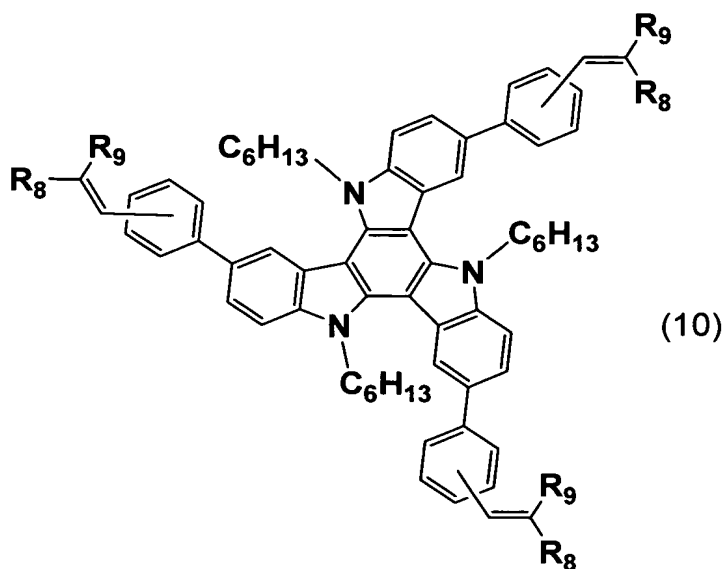


5 with a phosphorus oxyhalide.

[0052] to [0059]

[7] A process for producing a Sym-triindole derivative represented by the following general formula (10)

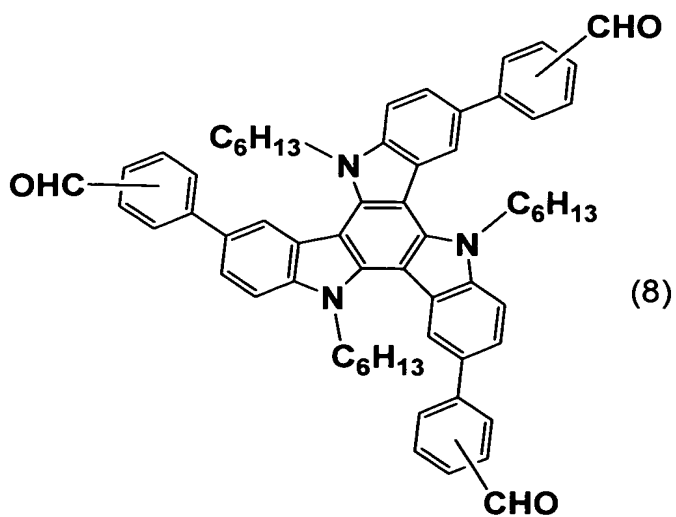
[formula 16]



(wherein R_8 is hydrogen or cyano group; R_9 is cyano group, carboxylic acid group, alkoxy carbonyl group, aryl group or substituted aryl group; and $-C_6H_{13}$ is n-hexyl group), which process comprises reacting a triindole derivative represented

5 by the following general formula (8)

[formula 14]



(wherein $-C_6H_{13}$ has the same definition as given above) with a methylene compound represented by the general formula (9)

[formula 15]

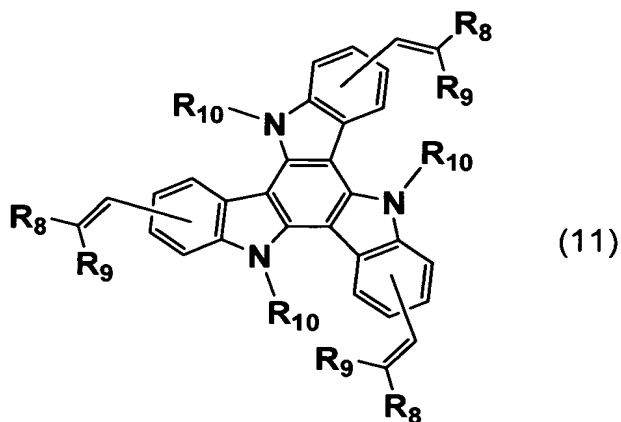


(wherein R_8 and R_9 have the same definitions as give above).

5 [0060] to [0063]

[8] A Sym-triindole vinyl derivative represented by the following general formula (11)

[formula 17]

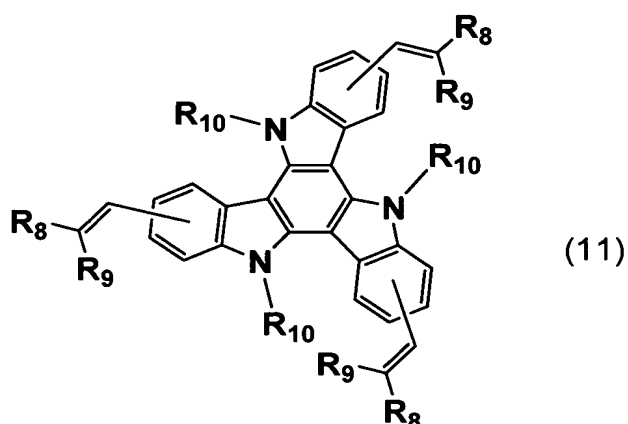


(wherein R_8 is hydrogen or cyano group; R_9 is cyano group, carboxylic acid group, ester group, aryl group or substituted aryl group; and R_{10} is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl group).

[0064] to [0079]

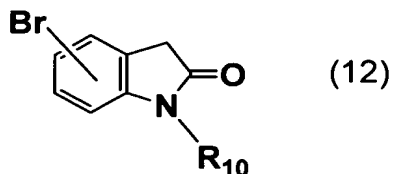
[9] A process for producing a Sym-triindole derivative represented by the following general formula (11)

[formula 22]



(wherein R₈ is hydrogen or cyano group; R₉ is cyano group,
 5 carboxylic acid group, ester group, aryl group or substituted
 aryl group; and R₁₀ is C2-C12 alkyl group, substituted C2-C12
 alkyl group or C2-C12 haloalkyl group), which process com-
 prises reacting an oxyindole compound represented by the fol-
 lowing general formula (12)

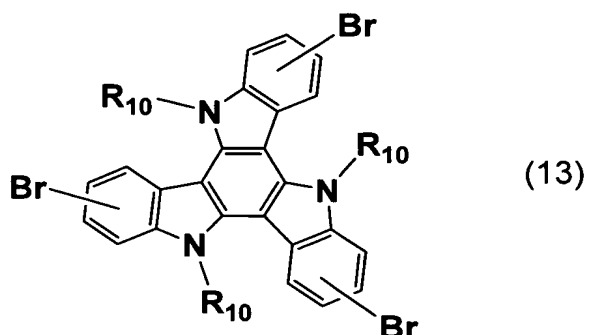
10 [formula 18]



(wherein R₁₀ is C2-C12 alkyl group, substituted C2-C12 alkyl
 group or C2-C12 haloalkyl group) with a phosphorus oxyhalide

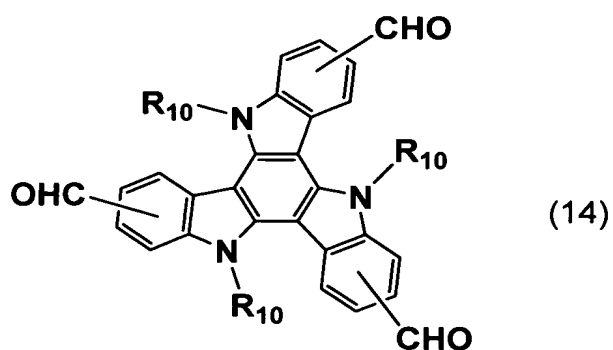
to obtain a Sym-bromotriindole derivative represented by the following general formula (13)

[formula 19]



(wherein R₁₀ has the same definition as given above), sub-
 5 jecting it to formylation with a formylating agent in the presence of butyllithium to obtain a Sym-formyltriindole derivative represented by the following general formula (14)

[formula 20]



(wherein R₁₀ has the same definition as given above), and re-
 10 acting it with a methylene compound represented by the following general formula (9)

[formula 21]

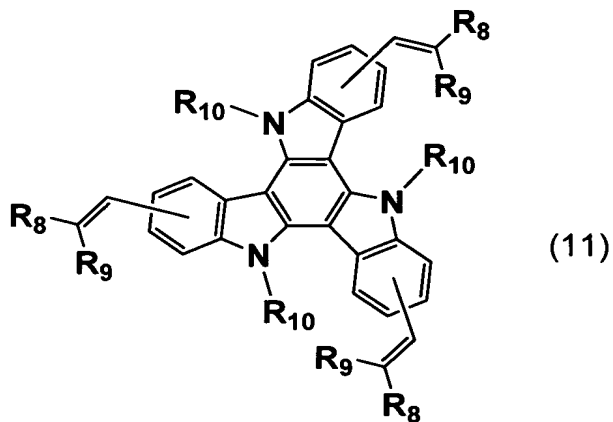


(wherein R₈ and R₉ have the same definitions as given above).

[0080] to [0089]

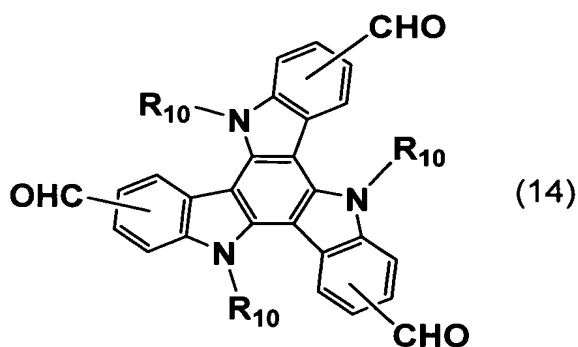
[10] A process for producing a Sym-triindole derivative represented by the following general formula (11)

[formula 25]



(wherein R₈ is hydrogen or cyano group; R₉ is cyano group, carboxylic acid group, alkoxy carbonyl group, aryl group or substituted aryl group; and R₁₀ is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl group), which process comprises reacting a Sym-formyltriindole derivative represented by the following general formula (14)

[formula 23]



(wherein R_{10} has the same definition as given above) with a methylene compound represented by the following general formula (9)

[formula 24]

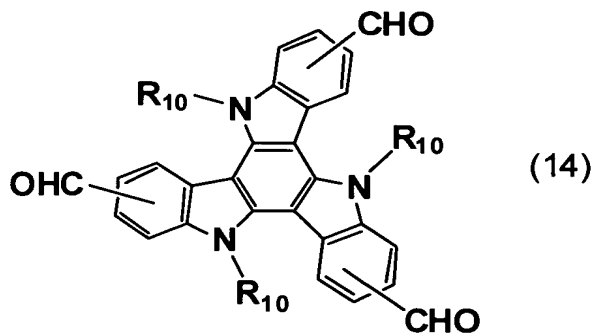


5 (wherein R_8 and R_9 have the same definitions as given above).

[0090] to [0096]

[11] A process for producing a Sym-formyltriindole derivative represented by the following general formula (14)

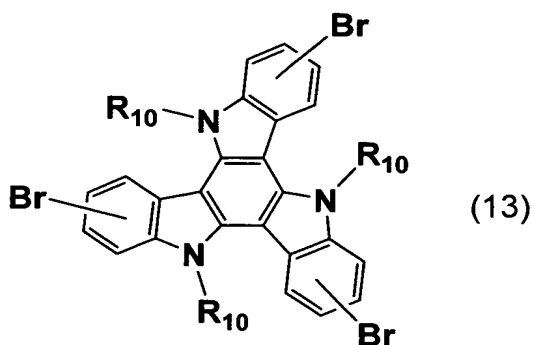
[formula 27]



10 (wherein R_{10} is C2-C12 alkyl group, C2-C12 substituted alkyl

group or C2-C12 haloalkyl group), which process comprises
subjecting a Sym-bromotriindole derivative represented by the
following general formula (13)

[formula 26]

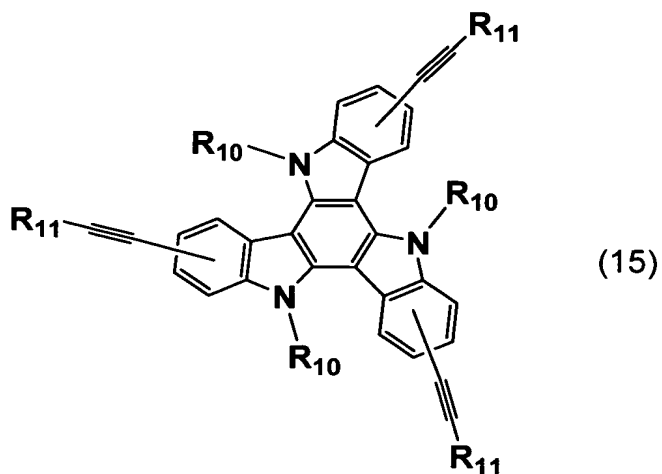


5 (wherein R₁₀ has the same definition as given above), to for-
mylation with a formylating agent in the presence of butyl-
lithium.

[0097] to [0100]

[12] A Sym-triindole derivative represented by the following
10 general formula (15)

[formula 28]

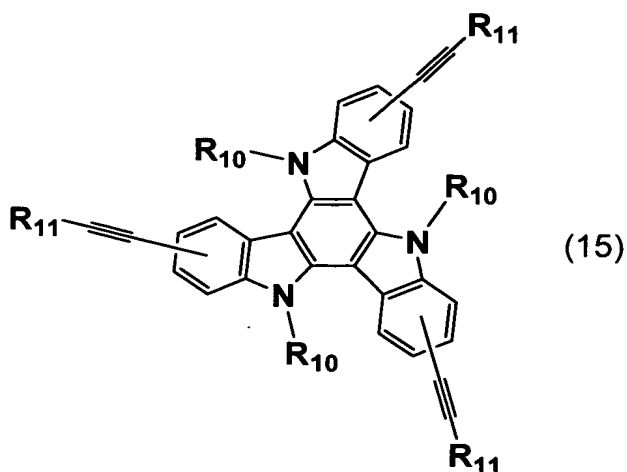


(wherein R_{10} is C2-C12 alkyl group, C2-C12 substituted alkyl group or C2-C12 haloalkyl group; and R_{11} is aryl group or substituted aryl group).

[0101] to [0110]

- 5 [13] A process for producing a Sym-triindole derivative represented by the following general formula (15)

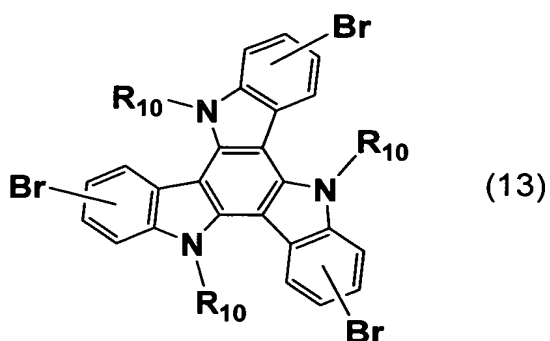
[formula 31]



(wherein R_{10} is C2-C12 alkyl group, substituted C2-C12 alkyl

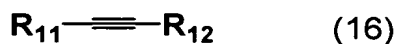
group or C2-C12 haloalkyl group; and R₁₁ is aryl group or substituted aryl group), which process comprises reacting a Sym-bromotriindole derivative represented by the following general formula (13)

5 [formula 29]



(wherein R₁₀ has the same definition as given above) with an acetylene derivative represented by the following general formula (16)

[formula 30]

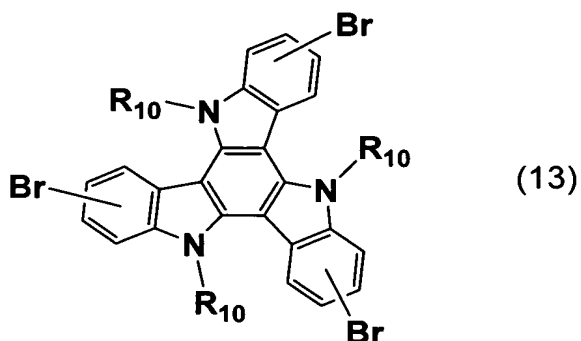


10 (wherein R₁₁ has the same definition as given above and R₁₂ is hydrogen or trimethylsilyl group).

[0111] to [0117]

[14] A process for producing a Sym-bromotriindole derivative represented by the following general formula (16)

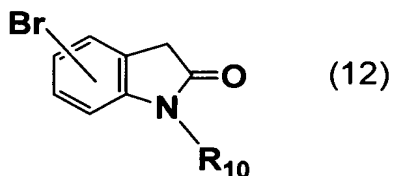
[formula 33]



(wherein R_{10} is C2-C12 alkyl group, substituted C2-C12 alkyl group or C2-C12 haloalkyl group), which process comprises re-

5 general formula (12)

[formula 32]



(wherein R_{10} has the same definition as given above).

[0118]

Explanation is made on the terms used in the present

10 specification.

[0119]

The expression of "C1-C6", etc. indicates that the group following the expression has 1 to 6 carbon atoms, in

the case of "C1-C6".

[0120]

"Halogen" indicates fluorine, chlorine, bromine or iodine.

5 [0121]

"C1-C6 alkyl group" indicates straight chain or branched chain C1-C6 alkyl group having 1 to 6 carbon atoms and, as specific examples thereof, there can be mentioned methyl group, ethyl group, n-propyl group, isopropyl group, 10 n-butyl group, isobutyl group, sec-butyl group, tert-butyl group, n-pentyl group, n-hexyl group and 3,3-dimethylbutyl group.

[0122]

"C2-C12 alkyl group" indicates straight chain or 15 branched chain C2-C12 alkyl group having 2 to 12 carbon atoms and, as specific examples thereof, there can be mentioned methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, tert-butyl group, n-pentyl group, n-hexyl group, 3,3-dimethylbutyl group, 20 n-heptyl group, n-octyl group, 2-ethylhexyl group, n-decyl

group and n-dodecyl group.

[0123]

"Aryl group" indicates aromatic group which may contain heterocyclic atom and which is a 5-or 6-membered single ring or a condensed ring formed by any condensation of 5-membered rings and/or 6-membered rings. There can be mentioned, for example, aromatic hydrocarbon groups of single ring or condensed ring, such as phenyl group, 1-naphthyl group, 2-naphthyl group, 1-anthranyl group, 2-anthranyl group, 9-anthranyl group, 1-phenanthryl group, 2-phenanthryl group, 9-phenanthryl group, 3-phenanthryl group, 4-phenanthryl, 1-pyrenyl group, 2-pyrenyl group, 4-pyrenyl group and the like; and aromatic heterocyclic ring group of single ring or condensed ring containing at least one nitrogen, oxygen or sulfur as heterocyclic atom, such as 2-pyridyl group, 3-pyridyl group, pyrrole group, pyrazolyl group, triazolyl group, quinolinyl group, indolyl group, isoindolyl group, thienyl group, benzothienyl group, furyl group, benzofuryl group, thiazolyl group, benzothiazolyl group, oxazolyl group, isoxazolyl group, benzoxazolyl group, thiadiazolyl group, benzothiadiazolyl

group and the like.

[0124]

“Substituted aryl group” indicates aryl group having the above-shown meaning, substituted independently with 1 to 5 7 groups selected from halogen having the above-mentioned meaning, cyano group and formyl group. There can be mentioned, for example, 2-chlorophenyl group, 4-cyanophenyl group and 4-formylphenyl group.

[0125]

10 “C1-C6 alkoxy group” indicates “(C1-C6 alkyl having the above-shown meaning)-O- group”. There can be mentioned, for example, methoxy group, ethoxy group, n-propoxy group, isopropoxy group, n-butoxy group, tert-butoxy group, n-pentyloxy group and n-hexyloxy group.

15 [0126]

“Aryloxy group” indicates “(aryl having the above-shown meaning)-O- group”. There can be mentioned, for example, phenoxy group.

[0127]

20 “C1-C6 haloalkyl group” indicates straight chain or

branched chain C1-C6 alkyl group substituted with 1 to 13
same or different halogens having the above-shown meaning.
There can be mentioned, for example, chloromethyl group, di-
chloromethyl group, trichloromethyl group and trifluoromethyl
5 group.

[0128]

"C2-C12 haloalkyl group" indicates straight chain or
branched chain C2-C12 alkyl group substituted with 1 to 13
same or different halogens having the above-shown meaning.
10 There can be mentioned, for example, chloroethyl group, 1,1-
dichloroethyl group, 2,2,2-trichloroethyl group and 2,2,2-
trifluoroethyl group.

[0129]

"Substituted C1-C6 alkyl group" indicates straight
15 chain or branched chain C1-C6 alkyl group substituted with 1
to 13 same or different hydroxy groups, C1-C6 alkoxy groups
having the above-shown meaning and aryl groups having the
above-shown meaning. There can be mentioned, for example,
hydroxymethyl group, methoxymethyl group and phenylethyl
20 group.

[0130]

“Substituted C2-C12 alkyl group” indicates straight chain or branched chain C2-C12 alkyl group substituted with 1 to 13 same or different hydroxy groups having the above-shown meaning, C1-C6 alkoxy groups having the above-shown meaning and aryl groups having the above-shown meaning. There can be mentioned, for example, hydroxyethyl group, methoxyethyl group and phenylethyl group.

[0131]

“C2-C6 alkenyl group” indicates straight chain or branched chain C2-C6 alkenyl group. There can be mentioned, for example, vinyl group, 1-propenyl group and 1-butenyl group.

[0132]

“Carboxyl group” indicates carboxyl group or carboxyl group of salt form. There can be mentioned, for example, groups such as carboxylic acid (-COOH), sodium carboxylate (-COONa), potassium carboxylate (-COOK), lithium carboxylate (-COOLi), pyridinium carboxylate (-COOH·pyridine) and the like.

[0133]

“Substituted C2-C6 alkenyl group” indicates straight chain or branched chain C2-C6 alkenyl group substituted with 1 to 11 same or different cyano groups having the above-shown meaning, carboxylic acid groups having the above-shown meaning, alkoxycarbonyl groups having the above-shown meaning, aryl groups having the above-shown meaning, and substituted aryl groups having the above-shown meaning. There can be mentioned, for example, 2,2-dicyanovinyl group, (2-cyano-2-ethoxycarbonyl)vinyl group, (2-cyano-2-carboxy)vinyl group, (2-cyano-2-phenyl)vinyl group, (2-cyano-2-(4-nitrophenyl))vinyl group, and (2-cyano-2-(4-pyridyl))vinyl group.

[0134]

“C2-C6 alkynyl group” indicates straight chain or branched chain C2-C6 alkynyl group. There can be mentioned, for example, ethynyl group, 1-propynyl group and 1-butynyl.

[0135]

“Substituted C2-C6 alkynyl group” indicates straight chain or branched chain C2-C6 alkynyl group substituted with

1 to 9 aryl groups having the above-shown meaning. There can be mentioned, for example, phenylethynyl group and (4-pyridyl)ethynyl group.

[0136]

5 "Acyl group" indicates "(C1-C6 alkyl having the above-shown meaning)-CO- group", "C1-C6 haloalkyl group having the above-shown meaning)-CO group, "aryl group having the above-shown meaning)-CO- group", or "substituted aryl group having the above-shown meaning)-CO- group". There can be mentioned,
10 for example, acetyl group, propionyl group and benzoyl group.

[0137]

"Mono-substituted amino group" indicates amino group mono-substituted with a C1-C6 alkyl group having the above-shown meaning or with an aryl group having the above-shown
15 meaning. There can be mentioned, for example, methylamino group, ethylamino group and phenylamino group.

[0138]

"Di-substituted amino group" indicates amino group di-substituted with same or different C1-C6 alkyl groups having
20 the above-shown meaning or same or different aryl groups hav-

ing the above-shown meaning. There can be mentioned, for example, dimethylamino group, diethylamino group and diphenylamino group.

[0139]

5 "Acylamino group" indicates amino group monosubstituted with a C1-C6 acyl group having the above-shown meaning. There can be mentioned, for example, acetylamino group, propionylamino group and butyrylamino group.

[0140]

10 "C1-C6 alkylsulfenyl group" indicates "(C1-C6 alkyl having the above-shown meaning)-S- group". There can be mentioned, for example, methylsulfenyl group (methylthio group) and ethylsulfenyl group (ethylthio group).

[0141]

15 "Arylsulfenyl group" indicates "(aryl having the above-shown meaning)-S- group". There can be mentioned, for example, phenylsulfenyl group (phenylthio group).

[0142]

20 "Substituted arylsulfenyl group" indicates "(substituted aryl group having the above-shown meaning)-S- group".

There can be mentioned, for example, (4-chlorophenyl)sulfenyl group ((4-chlorophenyl)thio group).

[0143]

"C1-C6 haloalkylsulfenyl group" indicates "(C1-C6 halo-
5 alkyl having the above-shown meaning)-S- group". There can be mentioned, for example, trifluoromethylsulfenyl group (trifluoromethylthio group).

[0144]

"Aralkylsulfenyl group" indicates "(aryl having the
10 above-shown meaning)-(alkyl having the above-shown meaning)-S- group" or "(substituted aryl having the above-shown meaning)-(alkyl having the above-shown meaning)-S- group". There can be mentioned, for example, benzylsulfenyl group (benzylthio group), (4-chlorobenzyl)sulfenyl group ((4-
15 chlorobenzyl)thio group).

[0145]

"C1-C6 alkylsulfinyl group" indicates "(C1-C6 alkyl
having the above-shown meaning)-SO- group". There can be mentioned, for example, methylsulfinyl group and ethyl-
20 sulfinyl group.

[0146]

"C1-C6 haloalkylsulfinyl group" indicates "(C1-C6 halo-alkyl having the above-shown meaning)-SO- group". There can be mentioned, for example, trifluoromethylsulfinyl group, 5 chloromethylsulfinyl group and 2-chloroethylsulfinyl group.

[0147]

"Arylsulfinyl group" indicates "(aryl having the above-shown meaning)-SO- group". There can be mentioned, for example, phenylsulfinyl group.

10 [0148]

"Substituted arylsulfonyl group" indicates "(substituted aryl having the above-shown meaning)-SO- group". There can be mentioned, for example, 4-chlorophenylsulfonyl group.

[0149]

15 "C1-C6 alkylsulfonyl group" indicates "(C1-C6 alkyl having the above-shown meaning)-SO₂- group". There can be mentioned, for example, methanesulfonyl group and ethanesulfonyl group.

[0150]

20 "C1-C6 haloalkylsulfonyl group" indicates "(C1-C6 halo-

alkyl having the above-shown meaning)-SO₂- group". There can be mentioned, for example, trifluoromethanesulfonyl group, chloromethanesulfonyl group and 2-chloroethanesulfonyl group.

[0151]

5 "Arylsulfonyl group" indicates "(aryl having the above-shown meaning)-SO₂- group". There can be mentioned, for example, phenylsulfonyl group.

[0152]

"Substituted arylsulfonyl group" indicates "(substituted aryl having the above-shown meaning)-SO₂- group".
10 There can be mentioned, for example, (4-chlorophenyl)sulfonyl group.

[0153]

"Sulfonic acid group" indicates -SO₂-OH group.

15 [0154]

C1-C6 alkoxy carbonyl group, indicates "(C1-C6 alkoxy having the above-shown meaning)-CO- group". There can be mentioned, for example, methoxycarbonyl group and ethoxycarbonyl group.

20 [0155]

"N-mono-substituted carbamoyl group" indicates carbamoyl group whose nitrogen atom is mono-substituted with a C1-C6 alkyl group having the above-shown meaning or with an aryl group having the above-shown meaning. There can be mentioned, for example, methylcarbamoyl group and phenylcarbamoyl group.

[0156]

"N,N-di-substituted carbamoyl group" indicates carbamoyl group whose nitrogen atom is di-substituted with C1-C6 alkyl groups having the above-shown meaning or with aryl groups having the above-shown meaning. There can be mentioned, for example, dimethylcarbamoyl group and diphenylcarbamoyl group.

[0157]

"Hydrazonomethyl group" indicates -CH=N-NH_2 group.

[0158]

"N-mono-substituted hydrazonomethyl group" indicates hydrazonomethyl group whose nitrogen atom is mono-substituted with a C1-C6 alkyl group having the above-shown meaning or with an aryl group having the above-shown meaning. There can

be mentioned, for example, methylhydrazonomethyl group and phenylhydrazonomethyl group.

[0159]

“N,N-di-substituted hydrazonomethyl group” indicates
5 hydrazonomethyl group whose nitrogen atom is di-substituted with C1-C6 alkyl groups having the above-shown meaning or with aryl groups having the above-shown meaning. There can be mentioned, for example, dimethylhydrazonomethyl group and diphenylhydrazonomethyl group.

10 [0160]

“Oximemethyl group (hydroxyiminomethyl group)” indicates -CH=N-OH group.

[0161]

“C1-C6 alkoxyiminomethyl group” indicates oxyimi-
15 nomethyl group whose oxygen atom is substituted with C1-C6 alkyl group having the above-shown meaning, and there can be mentioned, for example, methoxyiminomethyl group and ethoxyiminomethyl group.

[0162]

20 “Aryloxyiminomethyl group” indicates oxyimino-methyl

group whose oxygen atom is substituted with aryl group having the above-shown meaning. There can be mentioned, for example, phenoxyiminomethyl group.

[0163]

5 The present invention is described in detail below.

[0164]

 The present invention [1] lies in a Sym-triindole derivative represented by the general formula (1). In the general formula (1), R_1 , R_2 , R_3 and R_4 may be the same or different from each other and are each independently hydrogen, 10 halogen, C_1 - C_6 alkyl group, C_1 - C_6 haloalkyl group, substituted C_1 - C_6 alkyl group, C_2 - C_6 alkenyl group, substituted C_2 - C_6 alkenyl group, C_2 - C_6 alkynyl group, substituted C_2 - C_6 alkynyl group, hydroxyl group, C_1 - C_6 alkoxy group, aryloxy group, 15 amino group, mono-substituted amino group, di-substituted amino group, acylamino group, mercapto group, C_1 - C_6 alkylsulfenyl group, C_1 - C_6 haloalkylsulfenyl group, arylsulfenyl group, substituted arylfenyl group, C_1 - C_6 alkylsulfinyl group, C_1 - C_6 haloalkylsulfinyl group, arylsulfinyl group, substituted arylsulfinyl group, C_1 - C_6 alkylsulfonyl group, C_1 - C_6 20 tuted arylsulfonyl group, C_1 - C_6 alkylsulfonyl group, C_1 - C_6

haloalkylsulfonyl group, arylsulfonyl group, substituted
aryl sulfonyl group, sulfonic acid group (hydroxysulfonyl
group), aryl group, substituted aryl group, cyano group, ni-
tro group, formyl group, acyl group, carboxyl group, alkoxy-
5 carbonyl group, carbamoyl group, N-mono-substituted carbamoyl
group, N,N-di-substituted carbamoyl group, hydrazonomethyl
group ($-\text{CH}=\text{N}-\text{NH}_2$ group), N-mono-substituted hydrazonomethyl
group, N,N-di-substituted hydrazonomethyl group, oximemethyl
group (hydroxyiminomethyl group), alkoxyiminomethyl group or
10 aryloxyiminomethyl group;

R_5 is $\text{C}_2\text{-C}_{12}$ alkyl group, substituted $\text{C}_2\text{-C}_{12}$ alkyl group or $\text{C}_2\text{-C}_{12}$ haloalkyl group; in no event, all of R_1 , R_2 , R_3 and R_4 are hydrogen simultaneously.

[0165]

15 Therefore, as examples of the compound of the present
invention [1], there can be mentioned compounds shown in Ta-
ble 1. Incidentally, the abbreviations used in each of the
following Tables have the following meanings.

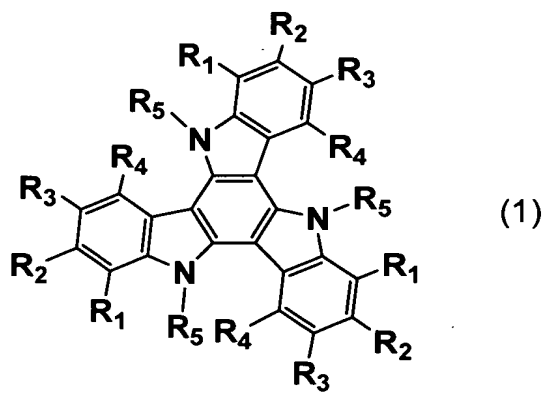
[0166]

20 MeO: methoxy group

	COOMe: methoxycarbonyl group
	COOEt: ethoxycarbonyl
	Ph: phenyl group
	NHBn: benzylamino group
5	SPh: phenylsulfenyl group (phenylthio group)
	SOPh: phenylsulfinyl group
	SO ₂ Ph: phenylsulfonyl group
	COMe: acetyl group
	CONHPh: phenylcarbamoyl group
10	NHCOPh: benzoylamino group
	vinyl: vinyl group
	Et: ethyl group
	n-Pr: n-propyl group
	Bu: n-butyl group
15	Pen: n-pentyl group
	n-Hex: n-hexyl group
	(2-Et)Hex: 2-ethylhexyl group
	dicyanovinyl: 2,2-dicyanovinyl group
	Py: pyridyl group
20	TMS-Ethynyl: trimethylsilylethynyl group

[0167]

[Formula 34]



[0168]

Table 1

Compound No.	R ₁	R ₂	R ₃	R ₄	R ₅	Melting point (°C)
1	Br	H	H	H	Et	205—207 161 160 185—187 243
2	H	Br	H	H	n-Pr	
3	H	H	Br	H	Bu	
4	H	H	H	Br	Penthyl	
5	H	H	Br	H	n-Hex	
6	H	H	Br	H	(2-Et)Hex	
7	H	H	Me	H	n-Hex	
8	H	H	CHO	H	n-Hex	
9	H	H	CHO	H	(2-Et)Hex	
10	H	H	CN	H	n-Hex	
11	H	H	COOMe	H	n-Hex	
12	H	COOH	H	H	n-Hex	
13	H	MeO	H	H	n-Hex	
14	H	H	NH ₂	H	n-Hex	
15	H	H	NHBn	H	n-Hex	
16	H	H	SPh	H	n-Hex	
17	H	H	SOPh	H	n-Hex	
18	H	H	SO ₂ Ph	H	n-Hex	
19	H	H	SO ₃ H	H	n-Hex	
20	H	H	COMe	H	n-Hex	
21	H	H	CONH ₂	H	n-Hex	
22	H	H	CONHPh	H	n-Hex	
23	H	H	NHCOPh	H	n-Hex	
24	H	H	NO ₂	H	n-Hex	
25	H	H	CF ₃	H	n-Hex	
26	H	H	Br	H	CF ₃ CH ₂	
27	H	H	TMS-Ethynyl	H	n-Hex	
28	H	H	Vinyl	H	n-Hex	

5 [0169]

The present invention [2] lies in a process for producing a substituted Sym-triindole derivative represented by the general formula (1), which comprises reacting an oxyindole represented by the general formula (2) with a phosphorus oxy-
5 halide.

[0170]

Firstly, description is made on the oxyindole represented by the general formula (2), used as a raw material of the present invention.

10 [0171]

In the general formula (2), R_1 , R_2 , R_3 and R_4 may be the same or different from each other and are each independently hydrogen, halogen, C_1 - C_6 alkyl group, C_1 - C_6 haloalkyl group, substituted C_1 - C_6 alkyl group, C_2 - C_6 alkenyl group, substituted
15 C_2 - C_6 alkenyl group, C_2 - C_6 alkynyl group, substituted C_2 - C_6 alkynyl group, hydroxyl group, C_1 - C_6 alkoxy group, aryloxy group, amino group, mono-substituted amino group, disubstituted amino group, acylamino group, mercapto group, C_1 - C_6 alkylsulfenyl group, C_1 - C_6 haloalkylsulfenyl group, aryl-
20 sulfenyl group, substituted arylfenyl group, C_1 - C_6 alkyl-

dibromooxyindole, N-ethyl-5-chlorooxyindole, N-ethyl-5-iodooxyindole, N-propyl-5-bromooxyindole, N-isopropyl-5-bromooxyindole, N-(n-hexyl)-5-bromooxyindole, N-(n-octyl)-5-bromooxyindole, N-(2-ethyl)hexyl-5-bromooxyindole, and N-(n-
5 hexyl)-5-methyloxyindole.

[0173]

The oxyindole used in the present invention is known, or can be produced by reacting a corresponding aniline with chloroacetyl chloride in the presence of aluminum chloride.

10 [0174]

As the phosphorus oxyhalide, there can be mentioned, for example, phosphorus oxychloride and phosphorus oxybromide. Ordinarily, phosphorus oxychloride is used preferably.

[0175]

15 The molar ratio of the oxyindole used as a raw material and the phosphorus oxyhalide may be any molar ratio as long as stirring is possible. However, the phosphorus oxyhalide is used in an amount of, for example, preferably 0.5 to 30 liters, more preferably 1 to 10 liters relative to 1 mole of
20 the oxyindole as raw material.

[0176]

The temperature of the reaction is not particularly restricted as long as the reaction proceeds at the temperature, but is preferred to be, for example, a range from 80°C to the
5 reflux temperature.

[0177]

The period of the reaction is not particularly restricted but is preferred to be, for example, 1 to 48 hours.

[0178]

10 Incidentally, a compound wherein R_1 , R_2 , R_3 and R_4 are hydrazonomethyl group, N-mono-substituted hydrazonomethyl group or N,N-di-substituted hydrazonomethyl group, can be produced by reacting a compound (obtained as above) wherein R_1 , R_2 , R_3 and R_4 are each formyl group, with hydrazine, an N-
15 mono-substituted hydrazine [typified by a C1-C6 alkylhydrazine (e.g. methylhydrazine or ethylhydrazine) or phenylhydrazine], or an N,N-di-substituted hydrazine [typified by a di(C1-C6 alkyl)hydrazine (e.g. N,N-dimethylhydrazine or N,N-diethylhydrazine) or diphenylhydrazine].

20 [0179]

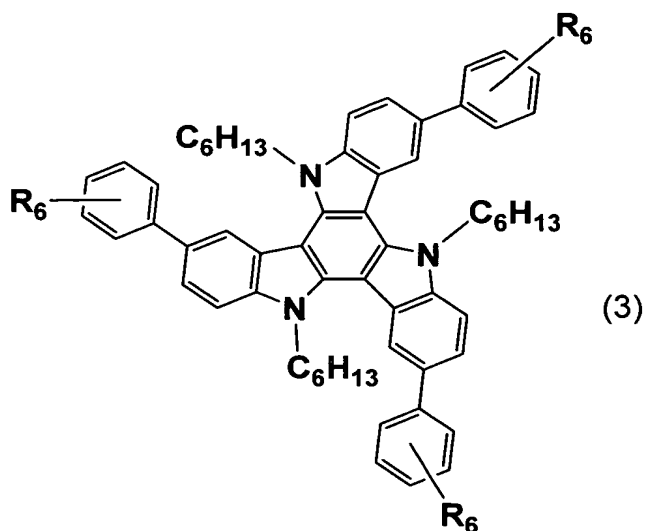
Also, a compound wherein R_1 , R_2 , R_3 and R_4 are oxime-methyl group (hydroxyiminomethyl group) or O-substituted oxyiminomethyl group (e.g. C1-C6 alkoxyiminomethyl group or aryloxyiminomethyl group), can be produced by reacting a compound (obtained as above) wherein R_1 , R_2 , R_3 and R_4 are each formyl group, with hydroxylamine or a salt thereof, or by reacting a compound (obtained as above) wherein R_1 , R_2 , R_3 and R_4 are each formyl group, with an O-substituted oxyamine such as C1-C6 alkoxyamine (alkanolamine) or salt thereof [e.g. methoxyamine (methanolamine) or salt thereof, or ethoxyamine (ethanolamine) or salt thereof], aryloxyamine (typified by phenoxyamine), or the like.

[0180]

The present invention [3] lies in a Sym-triindole derivative represented by the general formula (3). In the general formula (4), R_6 is hydrogen atom; formyl group; cyano group; dicyanovinyl group; ester group such as methoxycarbonyl group, ethoxycarbonyl group, propoxycarbonyl group or the like. Therefore, compounds shown in Table 2 can be mentioned as examples of the compound of the present invention.

[0181]

[Formula 35]



[0182]

Table 2

Compound No.	R ₆ (each of three R ₆ s)	Melting point(°C)
29	H	
30	4-CHO	245—257
31	4-COOEt	203—213
32	4-CN	297—303
33	4-dicyanovinyl	281—291
34	2-CHO	
35	3-CHO	
36	2-CN	
37	3-CN	

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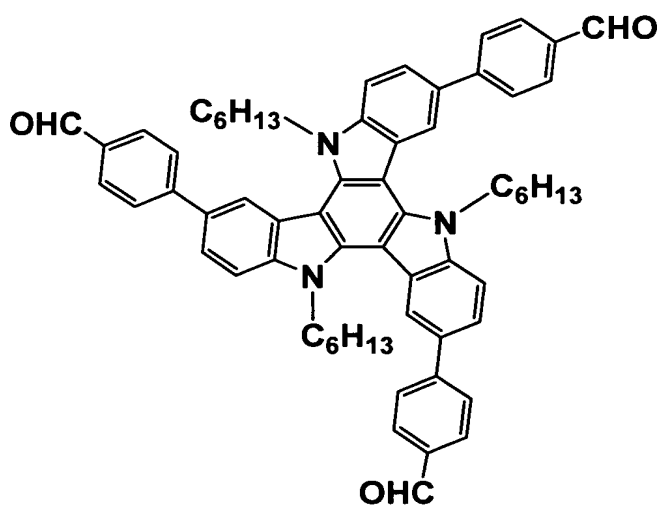
[0183]

As to Sym-N-(n-hexyl)-5-(4-formylphenyl)triindole (formula 39) which is a representative compound of the present invention, there are shown its absorption spectrum in a visi-

ble to ultraviolet region, in Fig. 1, and its fluorescent spectra in Fig. 2 (as measured in a dichloromethane solution) and Fig. 3 (as measured in a solid state).

[0184]

5 [Formula 36]



[0185]

The compound obtained by the present invention has a fluorescent spectrum from 400 nm to around 700 nm and accordingly it is expected that the compound is usable in organic
10 EL materials, solar cells, etc.

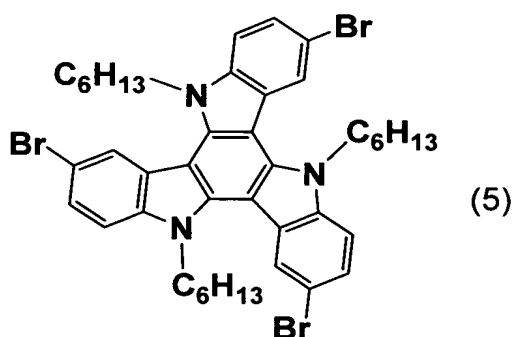
[0186] to [0188]

The present invention [4] lies in a process for producing a Sym-triindole derivative represented by the general

formula (7), which comprises reacting an N-(n-hexyl)-5-bromooxyindole represented by the general formula (4) with a phosphorus oxyhalide to obtain an N-(n-hexyl)-5-bromotriindole represented by the following general formula

5 (5)

[formula 37]



(first step) and reacting it with a boric acid compound represented by the general formula (6) (second step).

[0189]

10 Firstly, the first step of the present invention is described. The present step is a step for reacting an N-(n-hexyl)-5-bromooxyindole represented by the general formula (4) with a phosphorus oxyhalide to produce an N-(n-hexyl)-5-bromotriindole.

15 [0190]

The molar ratio of the oxyindole and the phosphorus oxyhalide both used as raw materials in the present step may be any molar ratio as long as stirring is possible. However, the amount of the phosphorus oxyhalide used as raw material is preferably 0.5 to 30 liters, more preferably 1 to 10 li-
5 ters relative to 1 mole of the oxyindole used as raw material.
[0191]

The temperature of the reaction is not particularly restricted as long as the reaction proceeds at the temperature, but is preferred to be, for example, a range from 80°C to the
10 reflux temperature.
[0192]

The period of the reaction is not particularly restricted but is preferred to be, for example, 1 to 48 hours.
15 [0193]

Then, the second step is described. The present step is a step for reacting the N-(n-hexyl)-5-bromooxyindole obtained in the previous step, with a boric acid compound represented by the general formula (6) to produce a Sym-
20 triindole derivative represented by the general formula (7).

[0194]

The boric acid compound represented by the general formula (6) (which is a raw material in the present step) is explained. In the general formula (6), R_6 is hydrogen atom, formyl group, cyano group, or alkoxycarbonyl group such as methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, isopropoxycarbonyl or the like; and R_a and R_b are each independently hydrogen atom, C1-C6 alkyl group, or optionally substituted phenyl and may be combined to each other to form a ring. (Therefore, R_a-B-R_b indicates boric acid group; straight chain or branched chain C1-C12 alkyl borate such as methoxyboric acid, ethoxyboric acid, isopropoxyboric acid or the like; or cyclic boric acid ester such as 4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl, 5,5-dimethyl-1,3,2-dioxaboroxan-2-yl or the like.

[0195]

Therefore, as specific examples of the boric acid compound represented by the general formula (6), usable in the second step reaction, there can be mentioned phenylboric acid, methyl phenylborate, ethyl phenylborate, isopropyl phenylbo-

rate, 2-formylphenylboric acid, 3-formylphenylboric acid, 4-formylphenylboric acid, methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzoate, ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzoate, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzonitrile, and 4-(5,5-dimethyl-1,3,2-dioxaboroxan-2-yl)benzaldehyde.

[0196]

In the reaction of the second step, the molar ratio of the boric acid compound represented by the general formula (6) and the N-(n-hexyl)-5-bromotriindole derivative may be any molar ratio; however, the preferred amount of the former is, for example, 3 to 15 moles relative to 1 mole of the N-(n-hexyl)-5-bromotriindole derivative.

[0197]

The reaction is conducted using a solvent. As to the solvent usable therein, there is no restriction as long as the solvent does not impair the present reaction. There are preferably used, for example, aromatic hydrocarbons such as benzene, toluene, xylene and the like; aprotic polar solvents such as dimethylformamide, diethylformamide, dimethy-

lacetamide and the like; cyclic ethers such as tetrahydrofuran (THF), dioxane and the like; chain ethers such as monoglyme, diglyme and the like; alcohols such as methanol, ethanol, butanol, ethylene glycol, propylene glycol, PEG-400
5 and the like; and water.

[0198]

The solvent used in the reaction may be a single solvent or a mixed solvent of any mixing ratio.

[0199]

10 The amount of the solvent used in the reaction may be any as long as stirring is possible; however, it is preferred to be, for example, 0.1 to 10 liters relative to 1 mole of the Sym-N-(n-hexyl)-5-bromotriindole (a raw material).

[0200]

15 The temperature of the reaction is not particularly restricted as long as the reaction proceeds at the temperature, but is preferred to be, for example, 40°C to the reflux temperature of the solvent used.

The period of the reaction is not particularly restricted but is, for example, 0.5 to 48 hours.
20

[0201]

The invention [5] is the second step of the invention [4] described above.

[0202]

5 The invention [6] is the first step of the invention [4] described above.

[0203]

The invention [7] lies in a process for producing a Sym-triindole derivative represented by the general formula (10), which comprises reacting a Sym-triindole derivative
10 represented by the general formula (8) with a methylene compound represented by the general formula (9).

[0204]

In the methylene compound represented by the general
15 formula (9), used in the reaction of the invention [7], R₈ is hydrogen atom or cyano group; and R₉ is cyano group, carboxylic acid group (e.g. carboxylic acid, sodium carboxylate, potassium carboxylate, lithium carboxylate or pyridinium carboxylate), alkoxycarbonyl group or aryloxycarbonyl group (e.g.
20 methoxycarbonyl, ethoxycarbonyl or phenoxycarbonyl), aryl

group (e.g. phenyl group, naphthyl group, 2-pyridyl group, 3-pyridyl group, 4-pyridyl group, 2-pyrimidine group, 4-pyrimidine group or triazine group), or substituted aryl group (e.g. 2-nitrophenyl group, 3-nitrophenyl group, 4-nitrophenyl group, 4-formylphenyl group, 4-cyanophenyl group or 6-methyl-2-pyridine group).

[0205]

Therefore, as the methylene compound represented by the general formula (9), usable in the reaction of the invention [7], there can be mentioned, for example, acetonitrile, malononitrile, methyl acetate, ethyl acetate, cyanoacetic acid, methyl cyanoacetate, ethyl cyanoacetate, phenyl cyanoacetate, 4-nitrophenyl cyanoacetate, 2-cyanomethylpyridine, 3-cyanomethylpyridine, 4-cyanomethylpyridine, 2-cyanomethylpyrimidine, benzyl cyanide and 4-nitrobenzyl cyanide.

[0206]

The molar ratio of the methylene compound represented by the general formula (9), usable in the reaction of the invention [7] may be any molar ratio as long as the reaction is

not impaired. However, the amount of the methylene compound is 0.1 to 30 moles, preferably 1 to 10 moles relative to 1 mole of the Sym-triindole derivative represented by the general formula (8).

5 [0207]

The reaction is ordinarily conducted using a solvent. As the solvent used in the reaction, there can be mentioned, for example, aprotic polar solvents such as dimethylformamide, dimethylacetamide, diethylacetamide, N-methylpyrrolidone,
10 N,N-dimethylimidazolinone, tetramethylurea and the like; aromatic hydrocarbons such as toluene, xylene, chlorobenzene and the like; chain or cyclic ethers such as diethyl ether, diisopropyl ether, tetrahydrofuran, dioxane and the like; acetic acid esters such as methyl acetate, ethyl acetate, butyl acetate and the like;
15 and nitriles such as acetonitrile and the like. The solvent used in the reaction may be a single solvent or a mixed solvent of any mixing ratio.

[0208]

The amount of the solvent used in the reaction may be
20 any as long as stirring is possible. However, the preferred

amount is, for example, 0.1 to 30 liters, preferably 0.5 to 10 liters relative to 1 mole of the Sym-triindole derivative of the general formula (8) which is a raw material.

[0209]

5 The temperature of the reaction may be any temperature as long as the reaction proceeds at the temperature, but is preferred to be, for example, -20°C to the reflux temperature of the solvent used.

[0210]

10 The period of the reaction is not particularly restricted but is preferred to be, for example, 1 to 48 hours.

[0211]

 The invention [8] lies in a Sym-vinyltriindole derivative represented by the general formula (11). In the general
15 formula (11), R₈ is hydrogen atom or cyano group; and R₉ is cyano group, carboxylic acid group (e.g. carboxylic acid, sodium carboxylate, potassium carboxylate, lithium carboxylate or pyridinium carboxylate), ester group (e.g. methyl ester, ethyl ester or phenyl ester), aryl group (e.g. phenyl group,
20 naphthyl group, 2-pyridyl group, 3-pyridyl group, 4-pyridyl

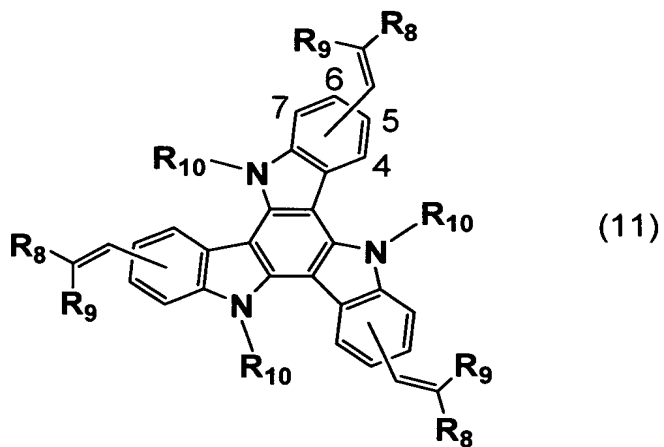
group, 2-pyrimidine group, 4-pyrimidine group or triazine group), or substituted aryl group (e.g. 2-nitrophenyl group, 3-nitrophenyl group, 4-nitrophenyl group, 4-formylphenyl group, 4-cyanophenyl group or 6-methyl-2-pyridine group).

5 [0212]

Therefore, compounds shown in Table 3 can be mentioned as the compound of the present invention.

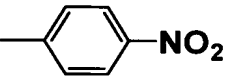
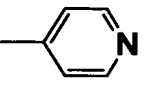
[0213]

[Formula 38]



10 [0214]

Table 3

Compound No.	Substitution position (each of three)	R ₈	R ₉	R ₁₀	Melting point (°C)
38	5	CN	CN	n-Hex	254—258
39	5	CN	COOEt	n-Hex	145—153
40	5	CN		n-Hex	300 or higher
41	5	CN		n-Hex	255—260
42	5	CN	CN	(2-Et)Hex	290(decomposed)
43	4	CN	CN	n-Hex	
44	6	CN	CN	n-Hex	
45	7	CN	CN	n-Hex	

[0215]

The invention [9] lies in a process for producing a Sym-triindole derivative represented by the general formula (11), which comprises reacting an oxyindole compound represented by the general formula (12) with a phosphorus oxyhalide to obtain a Sym-bromotriindole derivative represented by the general formula (13) (first step), reacting it with a formylating agent in the presence of butyllithium to obtain a Sym-formyltriindole derivative represented by the general formula (14) (second step), and reacting it with a methylene compound represented by the general formula (9) (third step).

[0216]

Firstly, description is made on the first step of the present invention, that is, the reaction of oxyindole with phosphorus oxyhalide.

5 [0217]

Firstly, explanation is made on the oxyindole compound represented by the general formula (12) used as a raw material.

[0218]

10 In the general formula (12), R_{10} is, for example, a straight chain or branched chain C2-C12 alkyl group such as ethyl group, n-propyl group, n-butyl group, n-pentyl group, n-hexyl group, isopropyl group, 2-ethylhexyl group or the like; or a straight chain or branched chain C2-C12 haloalkyl
15 group such as chloroethyl group, dichloroethyl group, trifluoroethyl group or the like.

[0219]

Therefore, as the oxyindole compound represented by the general formula (12), usable in the present invention, there
20 can be mentioned, for example, N-ethyl-4-bromooxyindole, N-

ethyl-5-bromooxyindole, N-ethyl-6-bromooxyindole, N-ethyl-7-bromooxyindole, N-(n-propyl)-5-bromooxyindole, N-(n-butyl)-5-bromooxyindole, N-(n-pentyl)-5-bromooxyindole, N-(n-hexyl)-5-bromooxyindole, N-(isopropyl)-5-bromooxyindole, and N-(2-ethylhexyl)-5-bromooxyindole.

[0220]

The oxyindole used in the present invention is known or can be produced by reacting a corresponding aniline with chloroacetyl chloride in the presence of aluminum chloride.

10 The molar ratio of the oxyindole used as a raw material and the phosphorus oxyhalide may be any molar ratio as long as stirring is possible. However, the preferred amount of the phosphorus oxyhalide is, for example, 0.5 to 30 liters, preferably 1 to 10 liters relative to 1 mole of the oxyindole.

15 [0221]

As the phosphorus oxyhalide, there can be mentioned, for example, phosphorus oxychloride and phosphorus oxybromide. Ordinarily, phosphorus oxychloride is used preferably.

[0222]

20 The temperature of the reaction may be any temperature

as long as the reaction proceeds at the temperature, but is preferred to be, for example, 80°C to the reflux temperature.

[0223]

The period of the reaction is not particularly restricted but is preferred to be, for example, 1 to 48 hours.

[0224]

Next, description is made on the formylation of the second step.

[0225]

The second step of the present invention is a step for reacting the Sym-bromoindole represented by the general formula (13) with a formylating agent in the presence of butyllithium to produce a Sym-formyltriindole represented by the general formula (14).

[0226]

As the formylating agent used in the present invention, there can be mentioned, for example, dimethylformamide, diethylformamide, formamide, N-formylpiperidine and N-formylpyrrolidine. Dimethylformamide and N-formylpiperidine are preferred. The molar ratio of the formylating agent and

the Sym-bromotriindole derivative of the general formula (13) (a raw material) may be any molar ratio as long as the reaction is not impaired; however, the amount of the formylating agent is, for example, 3 to 30 moles, preferably 3 to 9 moles relative to 1 mole of the Sym-bromotriindole derivative represented by the general formula (13).

[0227]

Butyllithium is simultaneously used in the present invention. The molar ratio of the butyllithium used in the present invention may be any molar ratio as long as the reaction is not impaired. However, the amount of the butyllithium is, for example, 3 to 15 moles, preferably 3 to 6 moles relative to 1 mole of the Sym-bromotriindole derivative represented by the general formula (13).

[0228]

The present step is generally conducted using a solvent. As the solvent used in the present step, there can be mentioned, for example, aromatic hydrocarbons such as toluene, xylene and the like; chain or cyclic ethers such as diethyl ether, diisopropyl ether, tetrahydrofuran (THF), dioxane and

the like; and hexamethylphosphoric triamide (HMPA). Tetrahydrofuran (THF) is preferred. The solvent used in the reaction may be a single solvent or a mixed solvent of any mixing ratio.

5 [0229]

The amount of the solvent used in the reaction may be any amount as long as stirring is possible, but is preferred to be, for example, 0.1 to 10 liters relative to 1 mole of the Sym-bromotriindole derivative which is a raw material.

10 [0230]

The temperature of the reaction may be any temperature as long as the reaction proceeds at the temperature, but is preferred to be, for example, -100°C to the reflux temperature of the solvent used, preferably -78 to 30°C .

15 The period of the reaction is not particularly restricted but is, for example, 0.5 to 48 hours.

[0231]

The third step is a step for reacting the Sym-formyltriindole derivative represented by the general formula
20 (14), obtained in the second step, with a methylene compound

represented by the general formula (9) to produce a Sym-triindole derivative represented by the general formula (11).

[0232]

In the methylene compound represented by the general
5 formula (9), used in the reaction of the third step, R₈ is
hydrogen atom or cyano group; and R₉ is cyano group, carbox-
ylic acid group (e.g. carboxylic acid, sodium carboxylate,
potassium carboxylate, lithium carboxylate or pyridinium car-
boxylate), alkoxycarbonyl group (e.g. methoxycarbonyl group
10 or ethoxycarbonyl group), aryloxycarbonyl group (e.g.
phenoxycarbonyl group), aryl group (e.g. aromatic heterocyc-
lic ring group of single ring or condensed ring containing
nitrogen, oxygen or sulfur as heterocyclic atom, such as
phenyl group, naphthyl group, 2-pyridyl group, 3-pyridyl
15 group, 4-pyridyl group, 2-pyrimidine group, 4-pyrimidine
group, triazine group, pyrazolyl group, triazolyl group, qui-
nolinyl group, indolyl group, isoindolyl group, thienyl group,
benzothienyl group, furyl group, benzofuryl group, thiazolyl
group, benzothiazolyl group, oxazolyl group, isoxazolyl group,
20 benzoxazolyl group, thiadiazolyl group, benzothiadiazolyl

group or the like] or substituted aryl group (e.g. 2-nitrophenyl group, 3-nitrophenyl group, 4-nitrophenyl group, 4-formylphenyl group, 4-cyanophenyl group or 6-methyl-2-pyridine group).

5 [0233]

Therefore, as the methylene compound represented by the general formula (9), usable in the reaction of the third step, there can be mentioned, for example, acetonitrile, malononitrile, methyl acetate, ethyl acetate, cyanoacetic acid, methyl cyanoacetate, ethyl cyanoacetate, phenyl cyanoacetate, (4-nitrophenyl) cyanoacetate, 2-cyanomethylpyridine, 3-cyanomethylpyridine, 4-cyanomethylpyridine, 2-cyanomethylpyrimidine, benzyl cyanide and 4-nitrobenzyl cyanide. The molar ratio of the methylene compound represented by the general formula (9), used in the reaction may be any molar ratio as long as the reaction is not impaired. However, the amount of the methylene compound is 0.1 to 30 moles, preferably 1 to 10 moles relative to 1 mole of the Sym-formyltriindole derivative represented by the general formula (14).

10
15
20

[0234]

The reaction is ordinarily conducted using a solvent. As the solvent used in the reaction, there can be mentioned, for example, aprotic polar solvents such as dimethylformamide, 5 dimethylacetamide, diethylacetamide, N-methylpyrrolidone, N,N-dimethylimidazolinone, tetramethylurea and the like; aromatic hydrocarbons such as toluene, xylene, chlorobenzene and the like; chain or cyclic ethers such as diethyl ether, diisopropyl ether, tetrahydrofuran (THF), dioxane and the like; 10 acetic acid esters such as methyl acetate, ethyl acetate, butyl acetate and the like; and nitriles such as acetonitrile and the like. The solvent used in the reaction may a single solvent or a mixed solvent of any mixing ratio.

[0235]

15 The amount of the solvent used in the reaction may be any as long as stirring is possible. However, the preferred amount is, for example, 0.1 to 30 liters, preferably 0.5 to 10 liters relative to 1 mole of the Sym-formyltriindole derivative of the general formula (14) which is a raw material.

20 [0236]

The temperature of the reaction may be any temperature as long as the reaction proceeds at the temperature, but is preferred to be, for example, -20°C to the reflux temperature of the solvent used.

5 [0237]

The period of the reaction is not particularly restricted but is preferred to be, for example, 1 to 48 hours.

[0238]

The invention [10] is described. This invention is the
10 third step of the invention [9].

[0239]

The invention [11] is described. This invention is the second step of the invention [9].

[0240]

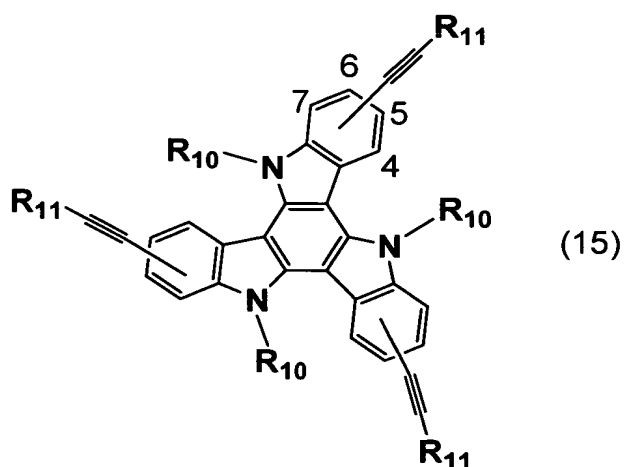
15 The invention [12] is described. This invention lies in a Sym-triindole derivative represented by the general formula (15). In the general formula (15), R_{10} has the same definition as given above; and R_{11} is, for example, aryl group (e.g. phenyl group, 2-pyridyl group, 3-pyridyl group,
20 4-pyridyl group or 2-pyrimidine group) or substituted aryl

group [e.g. 4-nitrophenyl group, 4-cyanophenyl group, or 4-(methoxycarbonyl)phenyl group].

Therefore, for example, compounds shown in Table 4 can be mentioned as the compound of the present invention.

5 [0241]

[Formula 39]



[0242]

Table 4

Compound No.	Substitution position (each of three)	R ₁₀	R ₁₁	Melting point (°C)
46	5	n-Hex	Ph	180—189
47	4	n-Hex	Ph	
48	6	n-Hex	Ph	
49	7	n-Hex	Ph	
50	5	(2-Et)Hex	Ph	
51	5	n-Hex	4-Py	
52	5	(2-Et)Hex	4-Py	

[0243]

The invention [13] is described.

[0244]

The present invention lies in a process for producing a Sym-triindole derivative represented by the general formula
5 (15), which comprises reacting a Sym-bromotriindole derivative represented by the general formula (13), with an acetylene derivative represented by the general formula (16).

[0245]

In the general formula (16), R_{11} is, for example, aryl
10 group (e.g. phenyl group, 2-pyridyl group, 3-pyridyl group, 4-pyridyl group or 2-pyrimidine group) or substituted aryl group [e.g. 4-nitrophenyl group, 4-cyanophenyl group or 4-(methoxycarbonyl)phenyl group]; and R_{12} is hydrogen atom or trimethylsilyl group.

15 [0246]

Therefore, as the acetylene derivative of the general formula (16) used in the reaction, there can be mentioned, for example, phenylacetylene, 1-phenyl-2-trimethylsilylacetylene, (pyridin-2-yl)acetylene, (pyridin-3-yl)acetylene,
20 (pyridin-4-yl)acetylene, (4-

cyanophenyl)acetylene, and 1-(pyridin-4-yl)-2-trimethylsilylacetylene.

[0247]

In the reaction, the molar ratio of the Sym-
5 bromotriindole derivative represented by the general formula
(13) and the acetylene derivative represented by the general
formula (16) may be any molar ratio. However, the amount of
the acetylene derivative represented by the general formula
(16) is preferably 3 to 10 moles per 1 mole of the Sym-
10 bromotriindole derivative represented by the general formula
(13).

[0248]

The reaction is conducted generally using a solvent.
As the solvent usable in the reaction, there can be mentioned,
15 for example, aromatic hydrocarbons such as toluene, xylene,
chlorobenzene and the like; halogenated aliphatic hydrocar-
bons such as dichloromethane, chloroform and the like;
aprotic polar solvents such as dimethylformamide, diethylfor-
mamide, N-methylpyrrolidone, dimethylacetamide and the like;
20 chain or cyclic ethers such as diethyl ether, tetrahydrofuran

(THF), dioxane and the like; alcohols such as methanol, ethanol and the like; polyethylene glycols such as PEG-400 and the like; nitriles such as acetonitrile and the like; nitrogen-containing bases such as pyrrolidine, triethylamine, 5 pyridine and the like; and water. The solvent used in the present reaction may be a single solvent or a mixed solvent of any mixing ratio.

[0249]

The amount of the solvent used in the reaction may be 10 any amount as long as stirring is possible; however, the amount is preferably 0.1 to 20 liters relative to 1 mole of the Sym-bromotriindole derivative of the general formula (13) which is a raw material.

[0250]

15 The temperature of the reaction may be any temperature as long as the reaction proceeds at the temperature, but is preferred to be, for example, 20°C to the reflux temperature of the solvent used.

[0251]

20 The period of the reaction is not particularly re-

stricted but is preferred to be, for example, 1 to 48 hours.

[0252]

The invention [14] is described. This invention is the first step of the invention [9]

5

Examples

[0253]

Next, the processes for producing the present invention compounds are specifically described by way of Examples.

10 However, the present invention is in no way restricted by these Examples.

[0254]

Example 1: Production of Sym-N-(n-hexyl)-5-bromotriindole

15 In a 500-ml, three-necked flask provided with a magnetic stirrer, a reflux condenser and a thermometer were placed 40 g of N-(n-hexyl)-5-bromooxyindole and 240 ml of phosphorus oxychloride. Refluxing was conducted with heating, for 8 hours, to give rise to a reaction. After the completion of the reaction, phosphorus oxychloride was recovered
20 under reduced pressure. To the resulting residue were added

water and a sodium hydroxide aqueous solution under cooling. The resulting crystals were collected by filtration and dissolved in 300 ml of toluene. The resulting solution was hot-filtered to remove the insolubles. The filtrate (toluene
5 layer) was washed with water and then concentrated. The concentrate (residue) was recrystallized (toluene : ethyl acetate = 1 : 9) to obtain 10.9 g of Sym-N-(n-hexyl)-5-bromotriindole. Yield: 29%

[0255]

10 Melting point: 205-207°C

FAB-Mass (NBA, Positive): $[(M+H)^+]$ = 835

$^1\text{H-NMR}$ (300 MHz, CDCl_3), δ (ppm):

0.84 (t, $J=6.6$ Hz, 9H), 1.20-1.41 (m, 18H),

1.88-2.20 (br, 6H), 4.59 (t, $J=8.1$ Hz, 6H),

15 7.41 (t, $J=8.7$ Hz, 3H), 7.52 (dd, $J=1.5, 8.7$ Hz, 3H),

8.21 (d, $J=1.5$ Hz, 3H)

[0256]

Example 2: Production of Sym-N-(n-hexyl)-5-phenyltriindole

In a 50-ml, three-necked flask provided with a magnetic
20 stirrer, a reflux condenser and a thermometer were placed, in

an argon atmosphere, 165 mg of Sym-N-(n-hexyl)-5-bromotriindole, 35 mg of tetrakis(triphenylphosphine) palladium (0) and 20 ml of toluene. Thereto were added a solution of 109 mg of phenylboronic acid in 5 ml of ethanol and 10 ml of a saturated sodium bicarbonate aqueous solution. Refluxing was conducted with heating, for 5 hours, to give rise to a reaction. After the completion of the reaction, the system was cooled to room temperature and filtered. To the resulting filtrate were added 50 ml of ethyl acetate and 30 ml of a saturated sodium chloride aqueous solution, for layer separation. The resulting ethyl acetate layer was concentrated. The concentrate was subjected to silica gel column chromatography (chloroform) to obtain 39 mg of Sym-N-(n-hexyl)-5-phenyltriindole. Yield: 23.8%

[0257]

FAB-Mass (NBA, positive): $[(M+H)^+]$ = 826

$^1\text{H-NMR}$ (270 MHz, CDCl_3), δ (ppm):

0.74 (t, $J=7.1$ Hz, 9H), 1.10-1.25 (m, 18H),

2.00-2.10 (br, 6H), 4.96 (t, $J=7.9$ Hz, 6H),

7.30-7.41 (m, 3H), 7.48-7.55 (m, 6H),

7.64-7.78 (m, 12H), 8.49 (s, 3H)

[0258]

Example 3: Production of Sym-N-(n-hexyl)-5-(4-formylphenyl)triindole

5 In Example 2, phenylboronic acid was replaced by 150 mg of 4-formylphenylboronic acid, whereby was obtained 35 mg of Sym-N-(n-hexyl)-5-(4-formylphenyl)triindole. Yield: 19.3%

[0259]

Melting point: 245-257°C

10 FAB-Mass (NBA, Positive): $[(M+H)^+]$ = 910

$^1\text{H-NMR}$ (270 MHz, CDCl_3), δ (ppm):

0.73 (t, $J=7.1$ Hz, 9H), 1.00-1.30 (m, 18H),

2.00-2.20 (br, 6H), 4.98 (t, $J=8.1$ Hz, 6H),

7.74 (s, 6H), 7.91 (d, $J=8.2$ Hz, 6H),

15 8.03 (d, $J=8.6$ Hz), 8.54 (s, 3H), 10.10 (s, 3H)

[0260]

Example 4: Production of Sym-N-(n-hexyl)-5-(4-ethoxycarbonylphenyl)triindole

In Example 2, phenylboronic acid was replaced by 247 mg
20 of ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-

yl)benzoate, whereby was obtained by 78 mg of Sym-N-(n-hexyl)-5-(4-ethoxycarbonylphenyl)triindole. Yield: 37.7%

[0261]

Melting point: 203-213°C

5 FAB-Mass (NBA, Positive): $[(M+H)^+]$ = 1042

$^1\text{H-NMR}$ (270 MHz, CDCl_3), δ (ppm):

0.74 (t, $J=7.1$ Hz, 6H), 1.02-1.28 (m, 18H),

1.45 (t, $J=6.9, 7.2$ Hz, 9H), 2.00-2.18 (br, 6H),

4.44 (q, $J=6.9, 7.2$ Hz, 6H), 4.92 (t, $J=7.9$ Hz, 6H),

10 7.68-7.74 (m, 6H), 7.80 (d, $J=8.2$ Hz, 6H),

8.19 (d, $J=8.2$ Hz, 6H), 8.50 (s, 3H)

[0262]

Example 5: Production of Sym-N-(n-hexyl)-5-(4-cyanophenyl)triindole

15 In Example 2, phenylboronic acid was replaced by 206 mg of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzonitrile, whereby was obtained 21.5 mg of Sym-N-(n-hexyl)-5-(4-cyanophenyl)triindole. Yield: 11.9%

[0263]

20 Melting point: 297-303°C

FAB-Mass (NBA, Positive): $[(M+H)^+]$ = 901

$^1\text{H-NMR}$ (270 MHz, CDCl_3), δ (ppm):

0.74 (t, $J=7.1$ Hz, 9H), 1.05-1.25 (m, 18H),

1.98-2.11 (br, 6H), 4.94 (t, $J=7.5$ Hz, 6H),

5 7.69 (d, $J=8.1$ Hz, 3H), 7.73 (d, $J=8.4$ Hz, 3H),

7.79 (d, $J=8.7$ Hz, 6H), 7.83 (d, $J=8.6$ Hz, 6H),

8.46 (s, 3H)

[0264]

Example 6: Production of Sym-N-(n-hexyl)-5-(4-(2,2-
10 dicyanovinyl)phenyl)triindole

In a 50-ml, three-necked flask provided with a magnetic stirrer, a reflux condenser and a thermometer were placed, in an argon atmosphere, 50 mg of Sym-N-(n-hexyl)-5-(4-formylphenyl)triindole, 16 mg of malononitrile and 5.5 ml of
15 THF. Thereto were added 0.165 mg of acetic acid and 2.3 mg of pyrrolidine. Stirring was conducted at room temperature for 4 hours to give rise to a reaction. After the completion of the reaction, the reaction mixture was concentrated. The concentrate (residue) was subjected to silica gel column
20 chromatography (chloroform) to obtain 25 mg of Sym-N-(n-

hexyl)-5-(4-(2,2-dicyanovinyl)phenyl)triindole. Yield: 43.2%

[0265]

Melting point: 281-291°C

FAB-Mass (NBA, Positive): $[(M+H)^+]$ = 1054

5 [0266]

Example 7: Production of Sym-N-(n-hexyl)-5-methyltriindole

In a 100-ml, three-necked flask provided with a magnetic stirrer, a reflux condenser and a thermometer were placed 7.60 g of N-(n-hexyl)-5-methyloxyindole and 60 ml of
10 phosphorus oxychloride. They were subjected to a reaction at 100°C for 11 hours. After the completion of the reaction, phosphorus oxychloride was recovered. Water was added and neutralization was made with sodium hydroxide. The resulting crystals were collected by filtration and dissolved in 250 ml
15 of toluene. The toluene solution was filtered to remove the insolubles. The filtrate was washed with water, dried with sodium sulfate, and concentrated, after which recrystallization (toluene : ethyl acetate = 1 : 9) was conducted to obtain 2.16 g of Sym-N-(n-hexyl)-5-methyltriindole. Yield: 31%

20 [0267]

Melting point: 160°C

EI-Mass: (M^+) = 639

$^1\text{H-NMR}$ (300 MHz, CDCl_3), δ (ppm):

0.83 (t, $J=6.6$ Hz, 9H), 1.20-1.45 (m, 18H),

5 2.03 (quint, $J=7.8$ Hz, 6H), 2.61 (s, 9H),

4.83 (t, $J=8.1$ Hz, 6H), 7.25 (bd, $J=8.4$ Hz, 3H),

7.50 (d, $J=8.4$ Hz, 3H), 8.06 (bs, 3H)

[0268]

Example 8: Production of Sym-N-(n-hexyl)-5-formyltriindole

10 In a 300-ml, three-necked flask provided with a magnetic stirrer, a reflux condenser and a thermometer were placed, in a nitrogen atmosphere, 1.5 g of Sym-N-(n-hexyl)-5-bromotriindole and 180 ml of tetrahydrofuran (THF). They were cooled to -78°C . Thereto was dropwise added 6.9 ml of
15 1.57 M n-butyllithium slowly and a reaction was allowed to take place for 1 hour at the same temperature. Then, 1.2 g of N-formylpiperidine was added slowly and a reaction was allowed to take place at -78°C for 1 hour. The reaction mixture was heated to 0°C and diluted hydrochloric acid was
20 added for hydrolysis. Then, extraction with toluene was con-

ducted. The toluene layer was dried with sodium sulfate and concentrated. The concentrate (residue) was recrystallized (tetrahydrofuran, THF) to obtain 1.01 g of Sym-N-(n-hexyl)-5-formyltriindole. Yield: 82%

5 [0269]

Melting point: 185-187°C

FAB-Mass (NBA, Positive): (M^+) = 681

IR (KBr, cm^{-1}): 1687

^1H -NMR (300 MHz, CDCl_3), δ (ppm):

10 0.80 (t, $J=7.2$ Hz, 9H), 1.20-1.40 (m, 18H),
2.03 (br, 6H), 4.93 (t, $J=7.8$ Hz, 6H),
7.72 (d, $J=8.7$ Hz, 3H), 8.02 (dd, $J=0.9, 8.4$ Hz, 3H),
8.77 (d, $J=1.2$ Hz, 3H), 10.17 (s, 3H)

Elemental analysis:

15 Calculated for $\text{C}_{45}\text{H}_{51}\text{N}_3\text{O}_3$ (%): C 79.26, H 7.54, N 6.16

Measured: C 79.20, H 7.49, N 6.19

[0270]

Example 9: Production of Sym-N-(n-hexyl)-5-(2,2-dicyanovinyl)triindole

20 In a 50-ml, three-necked flask provided with a magnetic

stirrer, a reflux condenser and a thermometer were placed
1.00 g of Sym-N-(n-hexyl)-5-formyltriindole, 0.437 g of ma-
lononitrile, 62.4 mg of piperidine, 4.40 mg of acetic acid
and 10 ml of tetrahydrofuran (THF). A reaction was conducted
5 at 50°C for 3 hours. After the completion of the reaction,
the solvent was removed by distillation. The resulting resi-
due was recrystallized using tetrahydrofuran (THF) to obtain
0.681 g of Sym-N-(n-hexyl)-5-(2,2-dicyanovinyl)triindole.
Yield: 56%

10 [0271]

Melting point: 254-258°C

FAB-Mass (NBA, Positive): $[(M+H)^+]$ = 826

IR (KBr, cm^{-1}): 2223

^1H -NMR (300 MHz, CDCl_3), δ (ppm):

15 0.69 (t, $J=7.2$ Hz, 9H), 1.05-1.30 (m, 18H),
1.82 (br, 6H), 5.09 (t, $J=7.2$ Hz, 6H),
7.79 (d, $J=8.7$ Hz, 3H), 7.94 (s, 3H),
7.97 (dd, $J=1.0, 8.7$ Hz, 3H), 8.95 (d, $J=1.0$ Hz, 3H)

Elemental analysis:

20 Calculated for $\text{C}_{54}\text{H}_{51}\text{N}_9$ (%): C 78.52, H 6.22, N 15.26

Measured:

C 78.30, H 6.26, N 15.16

[0272]

Example 10: Production of Sym-N-(n-hexyl)-(2-cyano-2-ethoxycarbonylvinyl)triindole

5 In a 50-ml, three-necked flask provided with a magnetic stirrer, a reflux condenser and a thermometer were placed 100 mg of Sym-N-(n-hexyl)-5-formyltriindole, 74.8 mg of ethyl cyanoacetate, 6.3 mg of piperidine and 15 ml of tetrahydrofuran (THF). A reaction was conducted at 50°C for 12 hours.

10 After the completion of the reaction, the solvent was removed by distillation. The residue was recrystallized using tetrahydrofuran (THF) to obtain 99.5 mg of Sym-N-(n-hexyl)-(2-cyano-2-ethoxycarbonylvinyl)triindole. Yield: 70%

[0273]

15 Melting point: 145-153°C

FAB-Mass (NBA, Positive): $[(M+H)^+]$ = 967

IR (KBr, cm^{-1}): 1590

$^1\text{H-NMR}$ (300 MHz, CDCl_3), δ (ppm):

0.68 (t, $J=7.2$ Hz, 9H), 1.05-1.18 (m, 18H),

20 1.45 (t, $J=7.2$ Hz, 9H), 1.78-1.91 (bs, 6H),

4.44 (q, J=7.2 Hz, 6H), 5.10 (t, J=8.1 Hz, 6H),
7.76 (d, J=8.7 Hz, 3H), 8.13 (dd, J=1.0, 8.7 Hz, 3H),
8.49 (s, 3H), 8.99 (d, J=1.0 Hz, 3H)

[0274]

5 Example 11: Production of Sym-N-(n-hexyl)-[2-cyano-2-(4-nitrophenyl)vinyl]triindole

In a 50-ml, three-necked flask provided with a magnetic stirrer, a reflux condenser and a thermometer were placed 100 mg of Sym-N-(n-hexyl)-5-formyltriindole, 107 mg of 4-nitrobenzyl cyanide, 6.3 mg of piperidine and 15 ml of tetrahydrofuran (THF). A reaction was conducted at 50°C for 12 hours. After the completion of the reaction, the resulting crystals were collected by filtration to obtain 117 mg of Sym-N-(n-hexyl)-[2-cyano-2-(4-nitrophenyl)vinyl]triindole.

15 [0275]

Melting point: 300°C or higher

FAB-Mass (NBA, Positive): $[(M+H)^+]$ = 1114

IR (KBr, cm^{-1}): 2212, 1340

[0276]

20 Example 12: Production of Sym-N-(n-hexyl)-[2-cyano-2-(4-

pyridyl)vinyl]triindole

In a 50-ml, three-necked flask provided with a magnetic stirrer, a reflux condenser and a thermometer were placed 100 mg of Sym-N-(n-hexyl)-5-formyltriindole, 120 mg of 4-
5 cyanomethylpyridine, 6.3 mg of piperidine and 15 ml of tetrahydrofuran (THF). A reaction was conducted at 50°C for 4 hours. After the completion of the reaction, the reaction mixture was subjected to silica gel column chromatography to obtain 131 mg of Sym-N-(n-hexyl)-[2-cyano-2-(4-
10 pyridyl)vinyl]triindole. Yield: 91%

[0277]

Melting point: 255-260°C

FAB-Mass (NBA, Positive): $[(M+H)^+]$ = 983

IR (KBr, cm^{-1}): 2210

15 ^1H -NMR (300 MHz, CDCl_3), δ (ppm):

0.64 (t, $J=7.2$ Hz, 9H), 0.90-1.14 (m, 18H),

1.82 (br, 6H), 4.81 (t, $J=7.2$ Hz, 6H),

7.52 (d, $J=8.7$ Hz, 3H), 7.59-7.61 (m, 6H), 7.82 (s, 3H),

7.96 (dd, $J=1.0, 8.7$ Hz, 3H), 8.63 (bs, 3H),

20 8.71-8.73 (m, 6H)

[0278]

Example 13: Production of Sym-N-(2-ethylhexyl)-5-bromotriindole

In a 100-ml, three-necked flask provided with a magnetic stirrer, a reflux condenser and a thermometer were placed 5.0 g of N-(2-ethylhexyl)-5-bromooxyindole and 30 ml of phosphorus oxychloride. A reaction was conducted at 100°C for 11 hours. After the completion of the reaction, phosphorus oxychloride was recovered under reduced pressure. To the residue were added water and sodium hydroxide for neutralization. Then, extraction with toluene was conducted. The toluene layer was concentrated and the concentrate was subjected to silica gel column chromatography to obtain 1.11 g of Sym-N-(2-ethylhexyl)-5-bromotriindole. Yield: 24%

[0279]

EI-MS (M^+): 918

Melting point: 161°C

$^1\text{H-NMR}$ (300 MHz, CDCl_3), δ (ppm):

0.26-0.33 (m, 9H), 0.56-0.65 (m, 9H),

0.74-1.04 (m, 24H), 1.61-1.72 (br, 3H),

4.07 (d, J=7.2 Hz, 6H), 7.42 (d, J=8.7 Hz, 3H),

7.58 (dd, J=1.5, 8.7 Hz, 3H), 7.75 (bs, 3H)

[0280]

Example 14: Production of Sym-N-(2-ethylhexyl)-5-
5 formyltriindole

In a 100-ml, three-necked flask provided with a magnetic stirrer, a reflux condenser and a thermometer were placed, in a nitrogen stream, 1.1 g of Sym-N-(2-ethylhexyl)-5-bromotriindole and 50 ml of tetrahydrofuran (THF). They
10 were cooled to -78°C. Thereto were dropwise added 4.2 ml of 1.57 M n-butyllithium slowly, followed by aging at the same temperature for 1 hour. Then, 0.74 g of N-formylpiperidine was added dropwise slowly. A reaction was conducted at -78°C for 1 hour. Thereafter, the system was heated to 0°C; di-
15 luted hydrochloric acid was added for hydrolysis; and extraction with toluene was conducted. The toluene layer was concentrated and the concentrate was subjected to silica gel column chromatography to obtain 0.80 g of Sym-N-(2-ethylhexyl)-5-formyltriindole. Yield: 87%

20 [0281]

Melting point: 243°C

FAB-Mass (NBA, Positive): (M^+) = 765

IR (KBr, cm^{-1}): 1684

^1H -NMR (300 MHz, CDCl_3), δ (ppm):

5 0.33-0.39 (m, 9H), 0.52-0.60 (m, 9H),
 0.61-0.96 (m, 24H), 1.74-1.88 (br, 3H),
 4.67 (d, $J=6.3$ Hz, 6H), 7.62 (d, $J=8.4$ Hz, 3H),
 8.06 (dd, $J=1.2, 8.4$ Hz, 3H), 8.51 (bs, 3H),
 10.26 (s, 3H)

10 [0282]

Example 15: Production of Sym-N-(2-ethylhexyl)-5-(2,2-dicyanovinyl)triindole

In a 500-ml, three-necked flask provided with a magnetic stirrer, a reflux condenser and a thermometer were placed 0.80 g of Sym-N-(2-ethylhexyl)-5-formyltriindole, 0.31 g of malononitrile, 62.4 mg piperidine and 150 ml of tetrahydrofuran (THF). A reaction was conducted at 50°C for 3 hours. After the completion of the reaction, the reaction mixture was concentrated. The residue was recrystallized using tetrahydrofuran (THF) to obtain 0.15 g of Sym-N-(2-ethylhexyl)-

15

20

5-(2,2-dicyanovinyl)triindole. Yield: 16%

[0283]

Melting point: 290°C (decomposed)

FAB-Mass (NBA, Positive): $[(M+H)^+]$ = 910

5 IR (KBr, cm^{-1}): 2224

^1H -NMR (300 MHz, CDCl_3), δ (ppm):

0.43-0.56 (m, 9H), 0.62-0.70 (m, 9H),

0.72-1.11 (m, 24H), 1.86-2.20 (br, 3H),

4.99-5.60 (m, 6H), 7.76 (d, $J=8.4\text{Hz}$, 3H),

10 7.93 (s, 3H), 9.11 (bs, 3H)

[0284]

Example 16: Production of Sym-N-(n-hexyl)-5-(phenylethynyl)triindole

In a 100-ml, three-necked flask provided with a magnetic stirrer, a reflux condenser and a thermometer were
15 placed, in a nitrogen stream, 100 mg of Sym-N-(n-hexyl)-5-bromotriindole, 8.35 mg of bistriphenylphosphine palladium dichloride, 2.27 mg of copper (I) iodide, 4 ml of triethylamine and 4 ml of toluene. A reaction was conducted at 70°C
20 for 9 hours. After the completion of the reaction, the reac-

tion mixture was cooled to room temperature and neutralized with diluted hydrochloric acid. Extraction with toluene was conducted. The organic layer was washed with water and a saturated sodium chloride aqueous solution. The toluene
5 layer was concentrated and the concentrate was subjected to silica gel column chromatography to obtain 10 mg of Sym-N-(n-hexyl)-5-(phenylethynyl)triindole. Yield: 9.3%

[0285]

Melting point: 180-189°C

10 IR (KBr, cm^{-1}): 2927, 1565, 1494

^1H -NMR (300 MHz, CDCl_3), δ (ppm):

0.758 (t, $J=7.2$ Hz, 9H), 1.15-1.50 (m, 18H),

2.00-2.17 (m, 6H), 4.79-4.87 (m, 6H), 7.34-7.42 (m, 9H),

7.56-7.66 (m, 12H), 8.418 (s, 3H)

15 [Industrial Applicability]

[0286]

The present invention provides a novel substituted Sym-triindole derivative and a process for production thereof.

The substituted Sym-triindole derivative is applicable to a

20 wide spectrum of uses, such as various electrification pre-

ventions, electrification controls, capacitors, batteries, chemical sensors, displays, organic EL materials, solar cells, photodiodes, phototransistors, nonlinear materials, photorefractive materials, rustproof agents, adhesives, fibers, antistatic paints, electrodeposition paints, plating primers, electric corrosion protections and the like.

[Brief Description of the Drawings]

[0287]

Fig. 1 shows an absorption spectrum in a visible-to-ultraviolet light region of Sym-N-(n-hexyl)-5-(4-formylphenyl)triindole (formula 36).

Fig. 2 is a fluorescent spectrum of Sym-N-(n-hexyl)-5-(4-formylphenyl)triindole (formula 36) in a dichloromethane solution state.

Fig. 3 is a fluorescent spectrum of Sym-N-(n-hexyl)-5-(4-formylphenyl)triindole (formula 36) in a solid state.

(File Name) Drawings

Fig. 1

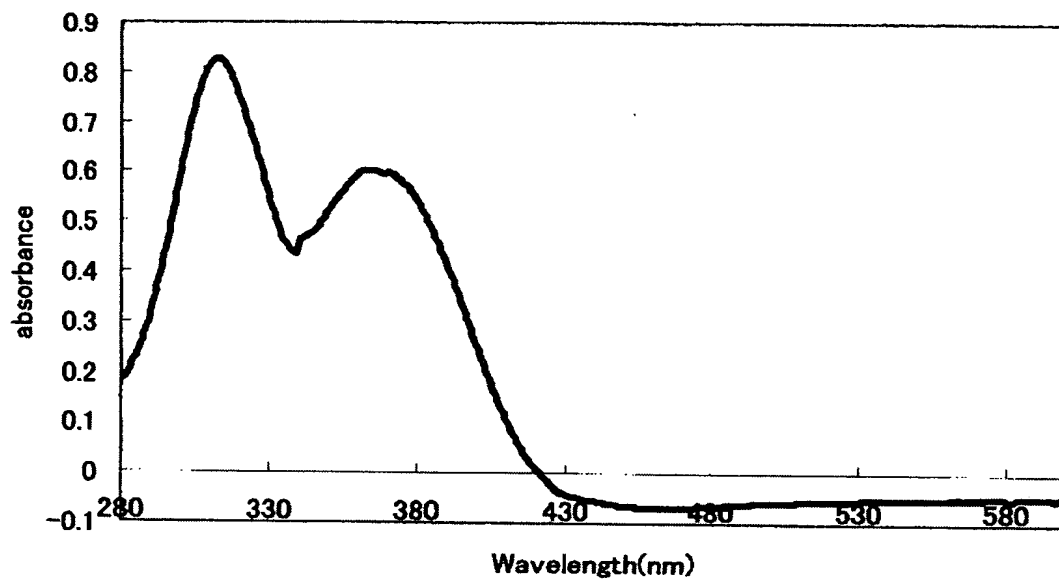
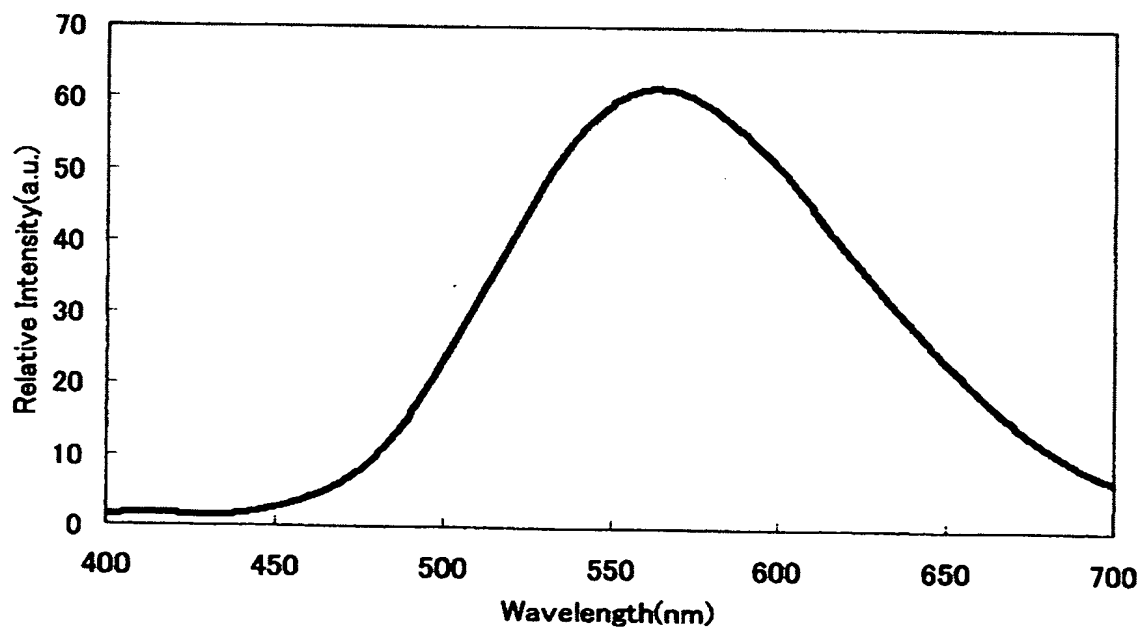
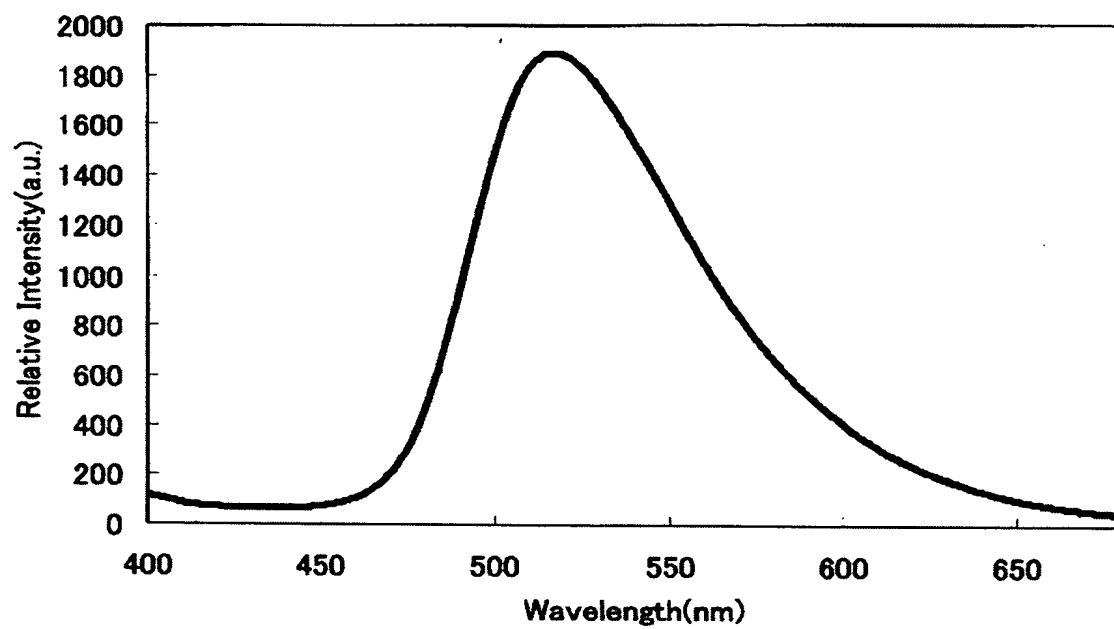


Fig. 2



F i g. 3



(File Name) Abstract of the Disclosure

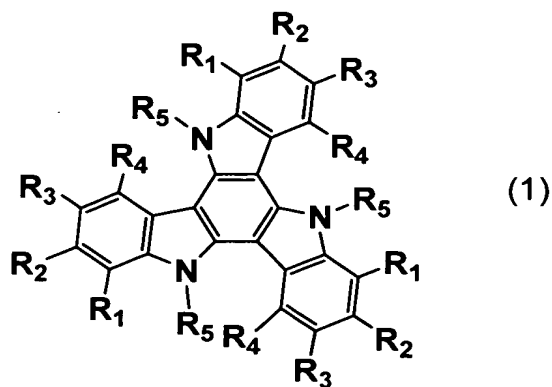
(Abstract)

(Object) To provide a novel substituted Sym-triindole deriva-
tive that is applicable to a wide spectrum of uses, such as
5 various electrification preventions, electrification controls,
capacitors, batteries, chemical sensors, displays, organic EL
materials, solar cells, photodiodes, phototransistors,
nonlinear materials and the like.

(Summary)

10 There is provided a substituted Sym-triindole deriva-
tive of the general formula (1)

[formula 1]



(wherein R₁, R₂, R₃ and R₄ are each independently hydrogen, a
halogen, a C1-C6 alkyl or the like, provided that, in no
15 event, all of R₁, R₂, R₃ and R₄ are hydrogen simultaneously).

(Advantages)

A novel substituted Sym-triindole derivative that is applicable to a wide spectrum of uses, such as various electrification preventions, electrification controls, capacitors, batteries, chemical sensors, displays, organic EL materials, solar cells, photodiodes, phototransistors, nonlinear materials, photorefractive materials, rustproof agents, adhesives, fibers, antistatic paints, electrodeposition paints, plating primers, electric corrosion protections and the like, is provided.

(Selected Drawing) Fig.2